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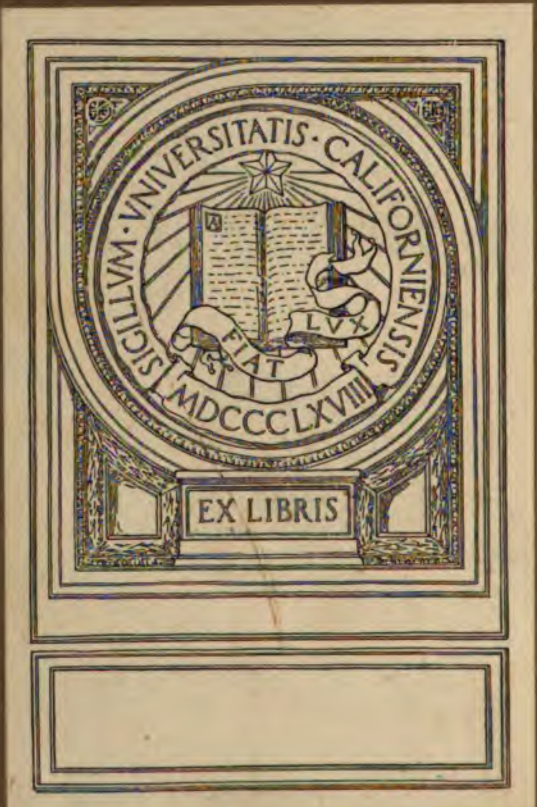

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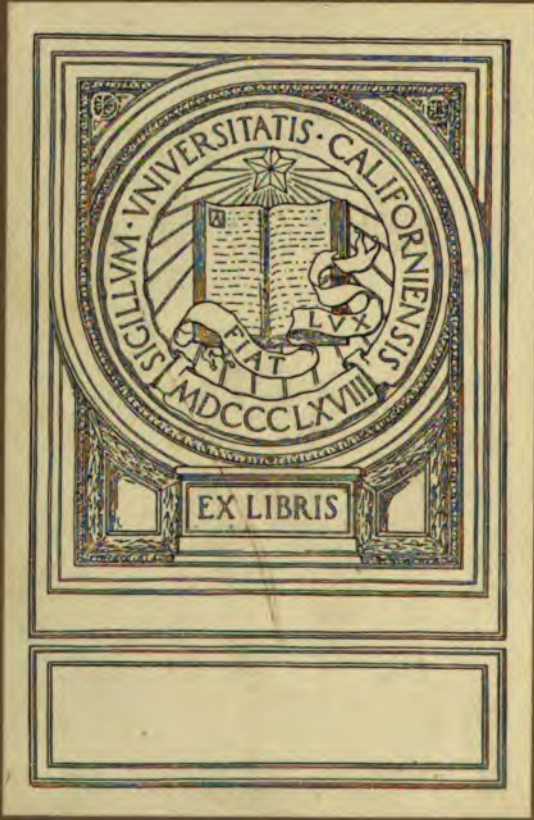
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THE PRINCIPLES OF THE PHASE THEORY

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THE PRINCIPLES OF THE PHASE THEORY

Heterogeneous Equilibria between Salts and their Aqueous Solutions

BY

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University of London, King's College.*

UNIV. OF
CALIFORNIA

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1920

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THIS BOOK IS DEDICATED, BY PERMISSION,

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F. A. H. SCHREINEMAKERS,

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AUTHOR'S PREFACE

The scope of this book is limited to the consideration of condensed systems which include only one liquid phase, and that the only phase of variable composition. I am convinced that a thorough study of the condensed system offers the easiest path to a true understanding of the methods of the Phase Theory, and I have therefore ventured to call this book "The Principles of the Phase Theory." It does not give a systematic development of the Phase Theory in its general application to heterogeneous systems in equilibrium, since the book is written primarily for the reader who is unfamiliar with the subject. A systematic treatment would involve, for example, a comparatively early discussion of the effects of variations, both in temperature and pressure, on the two-component system with liquid and vapour phases of variable composition; such a discussion must appear extremely difficult to the reader who is unfamiliar with the methods of the Phase Theory owing to the great number of the possible variables.

I have chosen throughout to illustrate the theory by means of condensed systems formed from salts and their aqueous solutions, since the majority of published experimental investigations fall within this category; the theory is, of course, equally applicable to all condensed systems.

If my treatment is not everywhere rigid, may I again advance the plea that I have written for readers unfamiliar with the subject; for the same reason, the treatment is not mathematical, nor have thermodynamic methods been used, either analytically or graphically.

I feel myself deeply indebted to Professor Schreinemakers for his volumes "Die ternären Gleichgewichte" in Roozeboom's work on Heterogeneous Equilibria, and for his publications in the chemical literature. I wish to express here my gratitude to him, and my admiration both of his beautiful and lucid theoretical work, and of his systematic experimental investigations.

My sincere thanks are also due to Mr. F. A. Freeth, whose pupil I was. I have been favoured with the opportunity of seeing a large number of his unpublished experimental researches, and of watching the development under his hand of many systems of great theoretical complexity. I owe it entirely to the inspiration of Mr. Freeth if I have succeeded anywhere in this book in conveying to the mind of the reader something of the beautiful generality which lies hidden beneath that hard-worked formula $P + F = C + 2$.

Finally, I wish to thank Miss Josephine Farrell for very valuable help in the preparation of the diagrams.

In addition to Professor Schreinemakers' publications, I have found Jänecke's book "Gesättigte Salzlösungen" and van't Hoff's "Ozeanische Salzablagerungen" of great value in the writing of this book.

DOUGLAS A. CLIBBENS.

KING'S COLLEGE,
LONDON.

March, .

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INTRODUCTION

BY

F. A. FREETH, O.B.E., M.Sc., F.I.C.

INTRODUCTION

THE science of Heterogeneous Equilibrium in its present form was developed by Roozeboom, who at the suggestion of van der Waals applied Gibbs's Phase Rule to elucidate difficulties which he had met in his early researches. The fact that this field has been almost entirely developed by Dutchmen is in keeping with the striking originality and thoroughness which characterise their scientific work in so many directions.

Since, with a few notable exceptions, singularly little attention has been paid to the subject in this country, the following criticisms may not be out of place. The point of view which regards Heterogeneous Equilibrium as the study of the relative quantities and compositions of the solid, liquid, and vapour phases into which a unit weight of matter is divided when subjected to varying pressure and temperature has not received sufficient notice in teaching. Far too much attention is concentrated on " curves " to the exclusion of the vital principle that every point in every diagram, whether on a curve or not, has a definite meaning. The fact that all the common forms of equilibria can be easily deduced by a system of graphical thermodynamics is not generally realised, although van Ryn van Alkemade's paper,[1] appealing as it does to the intuitive geometrical instinct, can be grasped, and its principles readily applied, by those who have no knowledge of mathematical analysis.

In the following survey the theoretical and experimental developments of systems up to five components are briefly described.

Since all the more complex one-component systems are now considered as at least pseudo-binary, we need not consider the true one-component system, as its form is so simple.

The two-component system is alone among those under discussion in having received anything like a full theoretical treatment, that is to say, a large number of the possible forms which may arise over all temperatures and pressures have been described. The first complete picture of everything that can happen in a simple two-component system is given by Roozeboom in the well-known space-model[1] which shows all heterogeneous equilibria from the critical temperatures down to those below which the type of equilibrium remains unchanged. The more complicated phenomena which arise when, for example, the solubility curve meets the critical curve, or when compounds occur, will be found in papers by Smits, Leopold, Scheffer, etc.[2]

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[1] Zeitsch. physikal Chem., vol. xi, p. 289.

As might be expected, condensed two-component systems are very well developed both theoretically and practically. Roozeboom's brilliant paper,[3] in which he deduced all the basic forms of mixed crystal equilibria, is almost the first and last word in the matter, and as for experimental examples, they literally run into hundreds, as a glance at the two-metal alloys, melts of two salts, and "solubilities," in Landolt and Börnstein's tables will show at once.

Two-component systems in which two liquid layers appear are also very numerous in the literature and have recently been dealt with in a special volume of Roozeboom's great book,[4] which is being completed by his pupils and colleagues.

The amount of experimental work which has been done on two-component systems restricted to liquid and vapour phases is enormous. Lecat's recently published book[5] contains a bibliography in which the names of seven hundred authors are mentioned. On the other hand, systems in which we have a solid, a liquid, and a vapour, or two solids and a vapour, are very few indeed. To sum up on the two-component system, we may say that experimental examples of equilibria between solid-liquid, liquid-liquid, and liquid-vapour are so numerous that the amount of work which has been done on solid-liquid-vapour and solid-vapour, both solids being assumed to have vapour pressures of the same order, is by comparison negligible. The corollary is, of course, that very few two-component systems are completely worked out.

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[1] Roozeboom, vol. ii, part I.

[2] See also Roozeboom, vol. ii, parts II. and III.

[3] Zeitsch. physikal. Chem., vol. xxx, p. 384.

[4] "Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre" (referred to simply as "Roozeboom" in other places).

[5] Lecat, "Azeotropisme," Brussels, Lamertin.

When we turn to the system of three components we soon find that an exhaustive theoretical treatment of form is not yet extant. The condensed system has been extensively worked out by the distinguished chemist to whom this work is dedicated. The simpler type of systems in which vapours appear is the subject of a long series of memoirs not yet completed,[1] but the number of cases which have been worked out theoretically is small as yet. The reason is simply that the number of possibilities is so great. "Solubilities," as they are often called, form a large portion of the experimental work. Three-component systems of the alloy and "melt" type are fairly numerous, but are not nearly so plentiful as those comprising the more easily manipulated substances like salts and water, and the organic liquids. The most surprising feature, however, is the absence of systematic research in a field which offers such wide possibilities. The reader will find a good deal on the condensed three-component system herewith, and in Roozeboom, vol. iii, parts I and II.

Four-component systems have only been treated generally in the condensed form, and that not completely. Schreinemakers's paper describing the simpler types[2] and his "Law of the Corresponding Isotherm" should be read, by all who are interested in the subject. The reciprocal salt pair is a special case among four-component systems, developed years ago by van't Hoff and his pupils; the treatment of this subject herewith will be found to be very complete.

Finally, in the five-component system only special cases like reciprocal salt pairs in which two of the five four-component systems involved have a common radicle have received a general treatment. The classical experimental examples are found in van't Hoff's work.

The literature of Heterogeneous Equilibrium is very scattered, and is not always easy to index, many important papers being published in journals which are not much read in England. The Proceedings of the Royal Academy of Sciences of

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[1] Schreinemakers, Verslage Akadamie Amsterdam 1913 *et seq.*

[2] Schreinemakers, Zeitsch. physikal. Chem., vol. lxv, p. 553.

Amsterdam contain many good papers. Useful bibliographies will be found in Jorissen and Ringer's " Life of Roozeboom " and in a small volume published in connection with the inauguration of a laboratory in Leiden in 1909.[1] The best classified bibliography is in the International Catalogue, Section D.

In conclusion, the writer wishes to put forward a plea for some form of standardisation in the tabulation and plotting of results. Anyone who has ever tried to unite the work of, say, three authors as a preparation for a complicated system will know that in many cases a quite unnecessary amount of re-calculation of results is required.

F. A. FREETH.

SANDIWAY.
March, 1920.

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[1] "The Inorganic Chemical Laboratory at Leiden." Jorissen. Sitjoff, Leiden.

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THE PRINCIPLES OF THE PHASE THEORY

CHAPTER I

THE PHASE THEORY AND ITS APPLICATION TO THE STUDY OF CONDENSED BINARY SYSTEMS

§ 1. A chemical system is said to be homogeneous when any part of it possesses the same chemical and physical properties as every other part.

We can prepare an aqueous salt solution in which the density of the lower layers is greater than the density of the upper layers. It is, however, an experimental fact that if such a solution be left to itself, the denser parts become gradually less dense, the lighter parts more dense, until all parts possess the same density, when no further change can be observed in the properties of the solution. The system is then said to be in a state of equilibrium, and it reaches this state when it is homogeneous. It is found, in the same way, that any part of a gaseous system which is in a state of equilibrium possesses the same physical and chemical properties as any other part, and the system is therefore homogeneous.

These statements are, however, subject to certain limitations. If the space occupied by the system is of very large dimensions, then the weight of the upper layers, acting upon the lower layers, causes the density of these lower layers to be greater than that of the upper layers; thus, for example, the earth's atmosphere, if it could be in a state of equilibrium, would not be homogeneous. On the other hand, if the space occupied by the system is of very small dimensions, then the effects produced by capillary forces may cause an appreciable deviation from strict homogeneity in a liquid system.

In practice, however, we always work with masses which are sufficiently small to enable us to neglect the disturbing action of gravitational forces, and are sufficiently large to enable us to neglect the disturbing action of capillary forces.

Let us next consider the system which is formed by a salt in contact with its saturated solution at a certain temperature. This system is also in a state of equilibrium, and it may remain for an indefinite time without the occurrence of any demonstrable change in its properties. Between the solid salt and the liquid solution there exists a physical surface of separation, which surface marks a discontinuity in the properties of the system. The system is therefore not homogeneous. Different parts of it show different physical and chemical properties, and it is said to be heterogeneous. Now it is clear that the heterogeneity of such a system does not lie in a continuous change from point to point in the properties of the system. It lies in the co-existence of a number of systems, each in itself homogeneous, but each separated from another by a physical surface; at this surface a sudden change occurs in the properties of parts of the system.

The homogeneous parts of a heterogeneous system are called the phases of the system. The saturated solution in contact with solid salt forms, therefore, a heterogeneous system of two phases. If in addition water vapour be present, then the system is one of the three phases: solution, solid salt, and vapour, each phase in itself homogeneous, but differing in physical and chemical properties from the others.

§ 2. The equilibrium in a heterogeneous system depends upon certain conditions, such as the temperature, in the sense that if these conditions are altered, the system ceases to be in a state of equilibrium, and a material change or reaction therefore occurs which results in the establishment of a new state of equilibrium. We will consider first the external conditions of equilibrium; these are the temperature and the pressure. As an example, we will choose again the heterogeneous system formed by a solid salt in contact with its saturated solution at a certain temperature T°. If the temperature is raised, let us say to the value $T + t^\circ$, then a transference of material from one phase to another will, in general, occur; such a transference is known as a phase reaction, and it may consist in this case in the dissolution of a certain amount of solid salt. The original system, which was in a state of equilibrium at T°, is no longer in equilibrium if the temperature is raised to $T + t^\circ$, and a phase reaction therefore takes place until a new state of equilibrium is reached. If the temperature of the system in equilibrium at T° is lowered to the value $T - t^\circ$, a new state of equilibrium will again be reached as the result of a phase reaction, which consists in the precipitation of solid salt from solution. The equilibrium is seen to be displaced by alteration of the temperature; at temperatures below T°, precipitation of solid salt occurs; at temperatures above T°, the opposite reaction, namely, dissolution of solid salt, occurs. At the temperature T° itself, these two opposing phase reactions are said to be in equilibrium. The state of the heterogeneous system in true equilibrium is not sufficiently characterised by the fact that the properties of the system do not alter perceptibly in the course of time. It is a further necessary condition that the same state shall be reached as the result of two opposing phase reactions, one of which takes place when the temperature of the system is raised from lower values to the value T°, and the other when the temperature is lowered from higher values to the same value. These conclusions result from the application of the general theory of chemical equilibrium to the particular case of the heterogeneous system.

In the same way, the pressure is a determining condition of the heterogeneous equilibrium. The effect of alterations in the pressure, upon the state of equilibrium of a heterogeneous system will be discussed later (§ 14).

§ 3. We shall now state two principles of fundamental importance for the phase theory.

First, if a heterogeneous system is in a state of equilibrium, then the various phases which form the system must, in themselves, be in a state of equilibrium.

Secondly, the equilibrium in the heterogeneous system is not dependent upon the actual amounts of the phases which form it.

For example, if from the system formed by a salt and its saturated solution at a given temperature, we remove a part of the liquid phase, then the homogeneous part which has been removed and the heterogeneous part which remains, still represent systems in equilibrium.

The equilibrium is, however, dependent upon the chemical compositions of the phases. The system formed by an unsaturated solution in equilibrium with water vapour at a certain temperature is under a certain pressure—called the vapour pressure of the solution. It is an experimental result that if the salt content of the solution is increased, the vapour pressure diminishes, and some water vapour must therefore condense. If the salt content is diminished, the vapour pressure rises and some water must therefore evaporate. We see that an alteration of the composition of the liquid phase, in a certain direction, displaces the equilibrium by causing a phase reaction to occur, whilst an alteration in the opposite direction causes the opposing phase reaction to occur. The chemical compositions of phases are, therefore, also to be considered as conditions which affect the equilibrium.

The compositions of the various phases of a heterogeneous system can be expressed in various ways. We must, however, first choose a certain number of substances in terms of which we can express the composition of every phase which is present in the system. These compositions can then be given by some mathematical form, as, for example, by the weight of each of these substances contained by 100 parts by weight of each of the phases in the system. Let us consider the case of a three-phase system formed by a solid anhydrous salt in contact with its saturated solution and water vapour, and let us denote the salt by S and water by W. We can then express the composition of each phase in terms of S and W by the following mathematical forms:

$$\begin{array}{ll} xS, & (100-x)W \text{ (liquid phase)}, \\ 100S, & 0W \text{ (solid phase)}, \\ 0S, & 100W \text{ (vapour phase)}. \end{array}$$

The total weight of each phase to which these expressions are referred is immaterial, since the equilibrium is not dependent upon the actual amounts of the phases; for convenience, therefore, we have chosen a total weight of 100. The substances in terms of which we express the compositions of phases of a heterogeneous system are called the components of the system. The choice of components is to some extent arbitrary. In the system just considered we have chosen the salt (S) and water (W) as components. We might, however, have chosen the salt, hydrogen, and oxygen as components, for we can express the compositions of phases by the following forms:

xS, yH_2, $(100 - \overline{x + y})\ O_2$ for the liquid phase,
$100S$, $0H_2$, $0O_2$ for the solid phase,
$0S$, zH_2, $(100 - z)O_2$ for the vapour phase.

The weight of hydrogen, y, in any liquid phase must, however, always be related to the weight of oxygen $(100 - \overline{x + y})$, in that phase, by the fact that these two components are always present in the same proportion in which they combine to form water, and the same relation is true of the weights of hydrogen and oxygen contained by any vapour phase. The absolute amounts of these two components are dependent upon one another; by altering the external conditions of equilibrium in this system, we cannot vary the amount of hydrogen in any phase without altering the amount of oxygen by a proportionate amount. This was not true of the two components salt and water. The proportion of salt to water contained by the liquid phase varies continuously as the temperature changes. The two components salt and water are, therefore, said to be independent components. The three components salt, hydrogen, and oxygen are not all independent components; two only are independent components, either salt and hydrogen, or salt and oxygen, and the weight of the third in any phase is fixed when the weights of the other two are given. Again, we might choose water and two ions as the components of the system. The absolute amounts of the two ions cannot, however, vary independently of each other in any phase. The weight of one ion in a given phase is already determined when the weight of the other is given. Two only of these three components are independent.

It must be carefully noticed that the components are said to be independent when the *absolute amount* of one, in any phase, can vary independently of the *absolute amount* of the other; we use the term "absolute amount" in contradistinction to the term "concentration." If the concentration of the salt in the liquid phase is x, that of the water is $100 - x$, and these two concentrations are not independent of each other, although water and the salt are independent components. This arises from the fact that the concentrations are referred always to the same total weight, namely, 100 parts of the liquid phase. The weight of salt contained in a liquid phase of undefined and varying total weight is in no way related to the weight of water in that phase; these two are independent components. The weight of hydrogen is, however, always equal to one-eighth that of the oxygen, whatever the total weight of the phase may be; these two are not independent components. If we restrict ourselves to the consideration of independent components only, we see that our choice must still be, to a certain extent, arbitrary. In the system which we have considered, we may choose the salt and water, the salt and hydrogen, the salt and oxygen, or water and one ion as independent components. The number of the independent components is, however, quite definite, and it does not share the arbitrary nature of the independent components themselves. Whatever choice we make in the present example, the number of independent components is two.

When we choose certain substances as the independent components of a system, we do not imply that these substances actually exist as molecular individuals within the phases. This may or may not be the case, and is quite immaterial, since we are not concerned with the state of homogeneous equilibrium within the phases, *i.e.*, with the actual molecular state of the constituents of the phases. If in our present example we choose the salt and hydrogen as independent components, we do not mean that elementary hydrogen exists as such in the phases of the system. We are not prevented from choosing the salt and water as independent components by the consideration that the salt may be electrolytically dissociated in the liquid phase, nor are we prevented from choosing water and one ion, by the consideration that the ion may not exist in the solid phase.

The only conditions which are attached to the choice of independent components are, first, that the compositions of all phases shall be capable of mathematical expression in terms of them, and, secondly, that it must be possible, by altering the conditions of equilibrium, to alter the absolute amounts of these components independently of each other, in at least one phase.

We are to consider as external conditions of equilibrium the temperature and pressure, and as internal conditions the concentrations of the independent components in the various phases. Systems of one independent component are called systems of the first order or unary systems; systems of two, three or four independent components are known as binary, ternary, or quaternary systems, and alternatively as systems of the second, third, or fourth order.

§ 4. It has already been seen that some kind of relation exists between the conditions of equilibrium in a heterogeneous system. Thus, when the temperature of the system formed by solid salt in contact with its saturated solution is altered, a new state of equilibrium is reached in which the liquid phase possesses a composition also differing from the original. We will study more closely the relations which exist between the conditions of heterogeneous equilibrium in the system formed by the two independent components water and an anhydrous salt. A variety of phases may coexist in this system, and we will assume in the first place that three phases are present in equilibrium: the salt, its saturated solution, and water vapour. It is a well-known experimental result that at a definite temperature a saturated salt solution has a definite composition and a definite vapour pressure. In other words, the conditions of equilibrium in the three-phase system, solid salt–saturated solution–vapour, are all fixed when the temperature is fixed; the internal conditions of equilibrium, given by the composition of the liquid phase, and the external conditions given by the temperature and pressure, cannot vary when the temperature is defined. If the temperature is slightly altered, the remaining equilibrium conditions will alter, namely the composition and the vapour pressure of the solution, but they will still be defined by the new temperature and will remain unaltered so long as this temperature is maintained. We are dealing here with a clearly characterised type of heterogeneous equilibrium; the equilibrium is said to be monovariant, and a system in this state of equilibrium is said to possess one degree of freedom. It is characteristic of a system in monovariant equilibrium that to every temperature there correspond definite values of the remaining equilibrium conditions; the temperature may be arbitrarily chosen, but when this has been done, the pressure and the compositions of phases become fixed. The binary system in three phases is a system with one degree of freedom. Suppose that, at constant temperature, the pressure is diminished by removing some of the vapour phase without altering the volume occupied by the system. Since the conditions of equilibrium cannot alter when the temperature is fixed, a phase reaction must take place which restores the original conditions. In the first place, therefore, water must evaporate to restore the original vapour pressure. This will, however, alter the composition of the liquid phase, and solid salt must therefore separate in order to retain the fixed composition. We see that the displacement of the equilibrium at constant temperature causes a phase reaction to occur which alters the relative weight proportions of the phases present, but not their actual compositions. The phase reaction is

$$\text{Solution} \rightarrow \text{Vapour} + \text{Solid},$$

the vapour and solid phases increase at the expense of the liquid phase, but this latter does not alter in composition.

If now the pressure be permanently diminished, this reaction, which tends to restore the original equilibrium conditions, will continue until all the water has been evaporated and all the salt has been separated in the solid state. It will continue until the liquid phase has disappeared, but during the whole of this process, and until the final disappearance of the liquid phase, the composition of the latter will not alter.

It is, therefore, a further characteristic of the system in monovariant equilibrium that if the conditions of equilibrium are permanently altered at constant temperature, a phase reaction occurs which results ultimately in the disappearance of one of the phases; during the course of the reaction, and until the disappearance of a phase, the relative quantities of the phases alter, but not their compositions.

§ 5. The existence of the system with one degree of freedom is limited to a certain temperature range. To every temperature within that range there correspond definite values for the remaining conditions of equilibrium. If the temperature of the three-phase system, salt–solution–vapour, be continuously raised, a point may be reached where all the solid salt has entered into solution. The solution will then become unsaturated, and the system one of two phases only, unsaturated solution and vapour. The following considerations will show that the resulting two-phase system is not in a state of monovariant equilibrium. Suppose that we have an unsaturated solution in equilibrium with water vapour at a certain temperature, and let the pressure be diminished whilst the temperature is kept constant. Some water will evaporate, and the composition of the solution will alter, since the concentration of the salt will be thereby increased. The resulting solution, being more concentrated, will possess a lower vapour pressure than the original solution, and can therefore remain in equilibrium with vapour at the new, diminished pressure. If the pressure be further diminished, still at constant temperature, a further alteration will occur in the composition of the liquid, and a state of equilibrium will again be attained at the altered pressure. We see here a very different behaviour from that of the three-phase system. At a fixed temperature, the pressure and the composition of the liquid phase can possess an indefinite number of different values, and the phase reaction which is induced at constant temperature, by an alteration of the pressure, does not result in the disappearance of a phase; the internal conditions of equilibrium readjust themselves to correspond with the new pressure. In order, therefore, to fix the internal conditions of equilibrium, it is necessary to fix, not only the temperature, but also the pressure. A system such as this is said to possess two degrees of freedom, or to be in a state of bivariant equilibrium. A system is in a state of bivariant equilibrium when it is necessary to define two of the conditions of equilibrium, in order to fix the remaining conditions.

The existence of the system with one degree of freedom is, therefore, limited on the side of high temperatures, in the case which we are considering, by the disappearance of a phase, and the formation of a system with two degrees of freedom.

§ 6. We will now consider the lower temperature limit to the existence of the system in monovariant equilibrium. If the temperature of the three-phase binary system, solid salt–solution–vapour, is continuously lowered, a point will be reached when ice as well as salt begins to separate. Ice and the solid salt do not form a homogeneous system, they are to be considered as forming two solid phases. At the temperature where the separation of ice begins, there are, therefore, four phases coexisting in the binary system, two solid phases, a liquid, and a vapour phase. If the abstraction of heat from the system is continued, the temperature will no longer continue to fall. Both ice and solid salt will, on the other hand, separate from the solution, and this phase reaction is such as to keep the temperature, the composition of the solution, and therefore also the pressure, constant. The temperature will not alter on the abstraction of heat until the whole of the solution has solidified to a conglomerate of ice and solid salt, when the system again becomes one of three phases. Similarly, if heat be added to the four-phase system, the temperature will not rise, but the solids will melt in such a way as to keep the temperature, the composition of the liquid, and the pressure constant, and none of these conditions of equilibrium will alter until one of the solid phases, ice or salt, has disappeared. We cannot alter any of the conditions of equilibrium of the four-phase binary system without removing one of the phases, and the system is therefore said to be in a state of invariant equilibrium, or to possess no degrees of freedom. We cannot choose arbitrarily any of the conditions of an invariant equilibrium, they are perfectly fixed. The equilibrium can exist only at one temperature, and if heat be added or abstracted, a phase reaction will occur at constant temperature; this reaction will alter the relative amounts of the phases, but will leave their compositions and the pressure of the vapour phase unchanged. Ultimately the phase reaction will result in the disappearance of a phase, and with the loss of a phase the system will regain a degree of freedom.

We see, therefore, that the existence of the system with one degree of freedom is limited, in the present case, on the side of lower temperatures, by the appearance of another phase, and the formation of a system with no degrees of freedom.

§ 7. We will summarise the results of the last three paragraphs. A study of the relations existing between the conditions of equilibrium in the binary system has led us to distinguish three types of heterogeneous equilibrium, namely, the monovariant, the bivariant, and the invariant. This classification of systems in heterogeneous equilibrium, according to the "variability" of the system, was first made by Bancroft, although the terms invariant, monovariant, etc., were first used by Trevor. We have seen, further, that the type of equilibrium, or the variability of the system, is determined by the number of the coexisting phases; the binary system in three phases possesses one degree of freedom, in two phases, two degrees of freedom, and in four phases, no degrees of freedom. These relations can be expressed in the form of a simple arithmetical rule known as the phase rule. If we denote the number of independent components in a heterogeneous system by C, the number of coexisting phases by P, then the number of degrees of freedom F, possessed by the system, is given by the following equation:

$$F = C + 2 - P.$$

The phase rule was deduced from theoretical considerations by W. Gibbs, and has been amply proved by subsequent experimental work. When the number of independent components in the system is fixed, the type of equilibrium is determined only by the number of coexisting phases. The system which we have discussed was one of two independent components and we have seen, in agreement with the rule, that when four phases coexist, the system possesses no degrees of freedom, *i.e.*, the equilibrium is invariant.

It is seen, however, that when the number of independent components may vary, this number is also a determining factor for the type of equilibrium.

It follows from the rule that if the number of independent components is greater than two, then the coexistence of more than four phases is necessary to produce a system in invariant equilibrium. In general, the number of phases must exceed the number of independent components by two, in order that a system of a given number of components may possess no degrees of freedom; the number of phases must exceed the number of independent components by one in order that the system may possess one degree of freedom, whilst to produce a system in bivariant equilibrium, the number of phases must be equal to that of the independent components.

Systems in heterogeneous equilibrium may therefore be classified, first, according to the number of independent components in the system (the order of the system), and, secondly, according to the degrees of freedom possessed by the system (the variability of the system); the latter is determined only by the number of coexisting phases when the order of the system is given.

Two gaseous phases can never coexist in one system, for it is a property of the gaseous state of aggregation that if two chemically indifferent gases be brought together, equilibrium is attained only when they have formed one homogeneous system. If the gases are not chemically indifferent, a heterogeneous system can result, since a solid or a liquid phase may be formed, but in no case can two gaseous phases be formed.

Two liquid phases can, however, exist in equilibrium with each other. For example, in the system formed by benzene and water there occur two liquid layers in equilibrium with each other, each layer in itself homogeneous but differing in physical and chemical properties from the other; each layer represents therefore a distinct liquid phase.

One or two cases only are known in which aqueous salt solutions separate into two layers, and we shall deal in this book only with heterogeneous systems containing one liquid phase.

When two homogeneous and chemically indifferent solids are brought together, they form, as a rule, two distinct phases. We must except from this rule solids which form together the type of homogeneous system known as a solid solution. Cases occur, namely, in which one solid dissolves in another to form a perfectly homogeneous solid system; the best known examples of this phenomenon are the isomorphous salt mixtures. We shall always assume the absence of isomorphous mixtures or mixed crystals, so that every component and every chemical combination of the components occurring as a solid in the system will represent a distinct phase.

§ 8. Following the classification given in the previous paragraph, we shall now consider in more detail the application of

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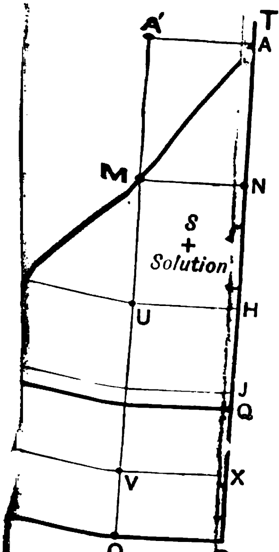

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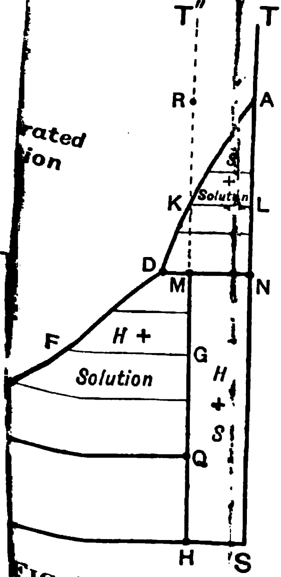

Fig. 5.

the phase theory to the study of heterogeneous equilibrium in binary systems which can be formed from the two components water and a salt. For this purpose, the various relations existing between the conditions of equilibrium which we have discussed in the foregoing paragraphs will be given a graphical representation.

Certain restrictions will, however, first be made.

We shall always assume that the salt is not volatile, a limitation which is justified for the majority of salts within ordinary temperature ranges. The vapour phase in the binary system is then of unvarying composition, since it consists always of pure water. We have already excluded the possibility of miscibility in the solid state, and every solid component, or chemical combination of components, will therefore also represent a phase of unvarying composition. The only phase the composition of which can vary will be the liquid phase, and its composition will be expressed by the weight of each of the components, water and salt, contained by a total of 100 parts by weight of the liquid. If x represents the weight of salt and $100-x$ the weight of water contained in 100 parts by weight of the liquid, then its composition will be given in the mathematical form:

$$xS,(100-x)W.$$

We will call x the concentration of the salt, and $100-x$ the concentration of the water in the liquid phase.

We must then consider, as controlling factors of the equilibrium in this system, the temperature, T, the pressure, P, and the concentration, x, of the salt, or $100-x$ of the water in the liquid phase; the two last are clearly dependent upon each other.

The relations which exist between three independent factors such as T, P, and x, cannot be represented graphically in one plane. For this purpose, a three dimensional or space figure must be used. In a plane figure, we can only represent the relations existing between two independent variables; we may, for example, represent in one plane picture the relations between T, the temperature, and P, the vapour pressure; or between x, the concentration of the salt in the liquid phase, and P, the vapour pressure ; or, finally, between T, the temperature, and x, the concentration of the salt.

The last of these three, the picture showing the relation between T and x, may, for example, be constructed by means of a rectangle such as $TWST'$ in Fig. 1. A point such as B, which lies on the side WT of this rectangle, represents pure water at a certain temperature, and this temperature is measured by the length, WB, on some suitable scale. The point W represents pure water at the lowest temperature at which we wish to study the system ; we may call this temperature the zero temperature. If we imagine the point B to start from W, and to move along the line WT in the direction of T, then it will represent, in its successive positions, pure water at continuously increasing temperatures, the actual temperature corresponding with any particular position being given by the distance of the point from the zero position W, measured according to the chosen scale. In the same way, a point such as C on the side ST' of the rectangle, represents the pure salt at a certain temperature, which is measured by the length SC on the same scale. The point S itself represents the pure salt at the zero temperature. The length of the side WS is chosen to represent 100 weight parts, and a point such as D, on this side, represents a certain mixture of W and S at the zero temperature. If the composition of the binary mixture D is given in the form

$$xS,\ (100 - x)W,$$

then the length WD is chosen equal to the salt concentration x, measured by the same scale on which WS equals 100 weight parts. Since WS equals 100, and WD equals x, it follows that DS is equal to $100 - x$, *i.e.*, it gives the concentration of water in the mixture. The point D divides the line WS into two parts, and we see that if the length of the part WS, further from S, is chosen to represent the concentration of the salt in the mixture D, then the length of the part DS, further from W, gives the concentration of water in that mixture. Following this rule, we see that the point W represents the limiting mixture in which the concentration of the salt is zero, the point S the limiting mixture in which the concentration of the water is zero; in other words, these two points truly represent pure water and pure salt respectively.

A point within the rectangle *TWST′* represents a mixture of the two components at a definite temperature and of a definite composition. The mixture may be either homogeneous or heterogeneous, it may consist of one phase only, or of a number of phases in equilibrium with each other; in the latter case, the mixture is said to be a phase complex or, more shortly, a complex. Thus the point *A* in Fig. 1 represents a binary phase or phase complex, and its temperature is measured by the length *AD*, the distance of the point from the side *WS* measured parallel to the temperature axis *WT* or *ST′*. Its composition is measured by the lengths of the sections into which the point divides the line *BAC*, which is drawn parallel to the concentration axis *WS*; *BA* gives the concentration of *S*, and *AC* that of water, in the phase or phase complex *A*. It is clear that all points on a line such as *BC*, which is parallel to the concentration axis, represent phases or complexes of varying composition but at one and the same temperature; thus the points *B*, *C*, and *A* represent, respectively, pure water, pure salt, and a certain mixture of the two, all at one temperature, which is measured by *WB*, *SC*, or *DA*. All points on a line such as *DA*, which is parallel to the temperature axis, represent phases or complexes of varying temperature, but of one and the same composition.

§ 9. We have shown how the state of the binary system $W - S$, at a given temperature, and with a liquid phase of given composition, can be represented by a point in a rectangle. A picture which shows the variations produced in x when T assumes different values is called a T, x picture; a picture which shows, by means of suitable geometrical construction, the variations produced in the pressure P when T assumes different values is called a T, P picture, and one which shows simultaneous variations of P with x, an x, P picture. Any one of these plane pictures by itself will, however, give an incomplete representation of the relations in the system. Let us suppose, as an example, that the three phases solid salt, solution, and vapour coexist in the system. The equilibrium will then be monovariant, and to a definite temperature, T_1, there will correspond a definite concentration, x_1, of the salt in the liquid phase. In the T, x picture the system, in this state, will be represented by a definite point for which $T = T_1$ and $x = x_1$. To the temperature T_1 there will, however, also correspond a definite vapour pressure P_1, but this will find no expression in the picture. To a different temperature, T_2, there will correspond another definite salt concentration, x_2, and a definite vapour pressure, P_2. The system in this state will be represented by another point for which $t = T_2$ and $x = x_2$, but the picture will not represent the fact that, to this point, there corresponds another definite vapour pressure, P_2. In other words, to every point in the picture there will correspond an unexpressed value for the vapour pressure, and this value will vary from point to point in the picture. The question now arises whether we can remove this incompleteness from the plane picture by making one of the conditions of equilibrium, let us say the pressure in the T, x picture, constant. In order to answer this question, we will reconsider the system composed of the three phases solid salt, solution, and vapour, which is in a state of monovariant equilibrium. To a certain temperature, T_1, there corresponds a certain salt concentration, x_1, and therefore, as we have seen, a definite point in the T, x picture. This three-phase system at the temperature T_1 can, however, only exist in equilibrium under a certain pressure, namely, the definite vapour pressure, P_1. If now we premise that the system is to be under a previously chosen constant pressure P, then it is clear that the three-phase system will not, in general, be stable. If, for example, the constant pressure P is higher than P_1, then a phase reaction must occur between the three phases which tends to reduce the pressure P to the value P_1. This phase reaction will consist in the condensation of vapour, and the simultaneous dissolution of salt to keep the composition of the liquid constant at the value x_1. If we maintain the pressure P, this phase reaction will lead to the complete disappearance of the vapour phase, provided that sufficient solid is present. The system will thus eventually become one of the two phases only, solid salt and saturated solution. It will then be in a state of bivariant equilibrium, and at the fixed temperature T, we may therefore choose arbitrarily our constant pressure P; the concentration of the salt x will then be fixed. We will choose our constant pressure P so that it is higher than the vapour pressure of any solution which can occur in the system. We shall thus eliminate the vapour phase, and we need consider only the equilibria between liquid and solid phases. A heterogeneous system which does not include a vapour phase is known as a condensed system, and we must inquire finally in what way the relation between the type of equilibrium and the number of coexisting phases is modified in the condensed binary system where the pressure is constant.

It follows, as we have seen, from the phase rule, that when four phases coexist in the binary system, all conditions of equilibrium are fixed, and among these the pressure under which the system may remain in equilibrium. Our constant pressure P is, however, higher than this invariant pressure, and four phases cannot therefore exist in equilibrium in the condensed binary system.

If three phases exist in the binary system where no restrictions are made, the equilibrium is monovariant, and we can therefore choose arbitrarily one of the conditions before the remainder become fixed. In the condensed binary system we have already done this, since we have chosen a constant pressure, and therefore all the conditions of equilibrium have become fixed. We may say that the binary system in three phases is in a state of invariant equilibrium *at constant pressure*; thus in the condensed system at constant pressure two solid phases and a liquid are in a state of invariant equilibrium.

Again, if two phases exist in the binary system where no restrictions are made, then the equilibrium is bivariant, and we can choose arbitrarily two of the conditions before the remainder become fixed. In the condensed system, we have already fixed the pressure, and at a given temperature the composition of the solution will therefore be fixed. In other words, the condensed binary system in two phases is in a state of monovariant equilibrium at constant pressure.

We have limited our study of the equilibria in the system by premising a constant pressure, with the following results. The vapour phase is eliminated, and the system becomes condensed. A picture showing the relations between the temperature T and the concentration x of the salt in solution will give complete information, since the pressure is everywhere the same. The number of coexisting phases necessary to produce equilibrium of a given type (invariant, monovariant, or bivariant) is less by one than the number which is necessary to produce the same type of equilibrium in the system, when no restrictions are made. We may say that we have disposed of one of the degrees of freedom of the system by fixing the pressure, and therefore reduced by one the number of phases necessary to produce equilibrium of a given type.

In systems of a higher order than the binary system, where the number of equilibrium conditions is greater than three, it is often necessary to limit the freedom of the system by fixing more than one of the equilibrium conditions. We have seen that the number of coexisting phases necessary for the production of equilibrium of a given type diminishes by one for each condition which has been fixed. It will then be necessary to qualify our description of the type of equilibrium by stating the conditions of equilibrium which are to be considered as fixed. Thus a true monovariant system will become an invariant system at constant pressure or at constant temperature, a true bivariant system will become a monovariant system at constant pressure or temperature, and an invariant system at constant pressure and temperature.

In this book we shall treat only of equilibria in condensed systems at constant pressure; we shall not consider the vapour phase except in some special cases, and the effect of pressure upon the state of equilibrium will be neglected. The effect of this theoretical limitation upon the practical value of the results obtained will be discussed later (§ 14). In view of this limitation, the reader is to understand that, when in future we describe an equilibrium as invariant, monovariant, or bivariant, we presuppose a constant pressure.

§ 10. The relations in the condensed binary system $W - S$, between the temperature T and the concentration x of the salt in the liquid phase, are represented graphically in Fig. 2, for the case in which no salt hydrate exists, and in which the solid salt can exist in one crystalline form only.

When three phases coexist in this system, the equilibrium is invariant, and all the equilibrium conditions are fixed. Since a vapour phase does not exist in the condensed system, the only three phases which may possibly coexist in equilibrium are solid salt, ice, and a solution. The composition of this solution and the temperature of the equilibrium will have definite values, and we will suppose that they are represented by the point *C* in Fig. 2. If the line *PCQ* be drawn parallel to *WS*, then the length *WP* measures the temperature of the invariant equilibrium, the length *PC* measures the concentration of the salt, and *CQ* that of water in the invariant solution. We shall call a point such as *C* which gives the conditions of invariant equilibrium a system invariant point.

Pure ice at the temperature of the invariant point is represented by the point *P*, which lies on the side *WT* of the rectangle, and at the same distance above the line *WS* as the point *C*. Pure salt at the temperature of the invariant point is represented by the point *Q* on the side *ST'*. The compositions of the three phases ice, solid salt, and solution, which are in equilibrium at the invariant temperature, are therefore represented by the points *P*, *Q*, and *C* respectively in Fig. 2. These three phases can only exist in equilibrium at the one temperature, and their compositions cannot vary from the values represented by the three points. If heat be abstracted from the three-phase system, the solution will deposit both ice and solid salt, and neither the temperature nor the composition of the solution can alter until the liquid phase has entirely solidified, *i.e.*, until it has been consumed by the following phase reaction :

$$\text{Solution } C \rightarrow \text{Ice} + S \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

The point *C* gives, therefore, the lowest temperature at which the liquid phase can exist in the system. When a system invariant point marks a lower temperature limit to the existence of the liquid phase, as it does in the case of the point *C*, it is called a eutectic point. When ice forms one of the solid phases in equilibrium with the liquid phase at the eutectic point, the latter is sometimes called a cryohydric point, but we shall always adhere to the term " eutectic point."

When the solution has been entirely consumed in the phase reaction (1), the temperature will begin to fall if the abstraction of heat be continued. We shall then be left at lower temperatures with the completely solid system formed by the two phases salt and ice. Every point in Fig. 2 below the constant temperature line PCQ represents, therefore, a complex of solid salt and ice. The condensed binary system in two phases is in a state of monovariant equilibrium; it can exist, therefore, over a range of temperature, but since in the present case both phases are solid, their compositions do not vary with the temperature.

A mixture of the composition and temperature represented by V will form, for example, a phase complex of solid ice represented at that temperature by the point R, and solid salt represented by the point X. A line such as RX joining two points which represent two phases in equilibrium is called a conjugation line, and it is clear that any point on the conjugation line RX represents a complex of the two phases represented at the terminal points of the line.

The space $PQSW$ is marked Ice + S in Fig. 2, since points in this space represent complexes of these two phases.

§ 11. The addition of heat to the three-phase system in invariant equilibrium at the eutectic point C will cause the solids to melt, *i.e.*, it will cause the following phase reaction to take place:

$$S + \text{Ice} \rightarrow \text{Solution } C \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Neither the temperature nor the composition of the liquid will alter until a phase has been removed by this reaction. Now according to the proportion by weight in which the two solid phases S and Ice were originally present, either one of these may be the first to disappear. If ice disappears first, we shall be left with the two-phase system S — Solution, whilst if the salt disappears first, we shall be left with the two-phase system Ice — Solution. Thus at temperatures above that of the eutectic point there may exist two different two-phase systems.

Of these, we will consider first the system composed of solid salt in equilibrium with solution. This system is monovariant and can therefore exist over a range of temperatures.

Both phases are not in this case of unvarying composition; the composition of the solution can alter, but, at a given temperature, it must possess a definite value. At a definite temperature, slightly above the eutectic temperature, the solution in equilibrium with solid salt will have a definite composition represented by the point E in Fig. 2. At a higher temperature, the composition of the solution will have a different but still definite value, such as that represented by the point D.

When a solution is in equilibrium with a solid, it is said to be saturated with that solid. Thus the points E, D, M represent the compositions of saturated solutions of the salt at definite temperatures, and they lie on a continuous curve $CEDMA$, which diverges from the eutectic point, and is called the polythermal saturation curve of the salt. It is characteristic of this polythermal saturation curve, that all points on it represent the compositions of solutions saturated, or in equilibrium, with solid salt at different temperatures. Since, in general, the concentration of salt in solutions saturated with solid salt rises with the temperature, the saturation curve of the salt will approach the side ST' of the rectangle which represents pure salt. It will reach its upper temperature limit at the point A where it cuts this side. Since the point A lies on the saturation curve, it represents a liquid phase in equilibrium with solid salt, but since it lies on the side ST', it also represents pure salt. At the temperature corresponding with the point A the pure liquid salt is therefore in equilibrium with solid salt or, in other words, the point A gives the melting point of the pure salt.

At the eutectic point C, the two solids, salt and ice, melt at constant temperature to a binary solution of definite composition. The eutectic temperature is therefore characteristic of the binary system $W - S$, in the same sense that the melting temperature of the pure salt is characteristic of the unary system S. The polythermal saturation curve of the salt extends then from the eutectic point, or the common melting point of S + Ice in the binary system $W - S$, to the melting point of S in the unary system S.[1]

At temperatures below the eutectic point, solutions cannot exist, and at temperatures above the melting point of S, the solid salt cannot exist.

The mixture represented by U in Fig. 2 clearly contains a greater proportion of salt than does the saturated solution D at the same temperature. If the mixture is in a state of true equilibrium, it must therefore consist of a phase complex of the solution *D* and the solid salt, which is represented at this temperature by the point *H*. The line *DH* is a conjugation line, and we see again that any point on it represents a complex of the two phases represented by its terminal points. In the same way, the saturated solution represented by *M* is in equilibrium with solid salt at the same temperature, represented by *N*, and any point on the conjugation line *MN* represents a complex of these two phases.

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[1] Certain necessary restrictions will be made later (§ 13).

In general, all points in the area *CAQ*, marked *S* + Solution in Fig. 2, represent complexes of two phases, namely solid salt and a solution on the saturation curve *CA*.

Points in this area may, however, also represent supersaturated solutions, *i.e.*, solutions in which the concentration of the salt is greater than the concentration of the salt in the saturated solution. The supersaturated solution is, in itself, stable, but on the addition of a crystal of the solid salt *S*, the state of stability is lost. The excess of salt above that necessary to form a saturated solution separates out, and the phase complex is formed, consisting of the solid salt in contact with a saturated solution. A supersaturated solution is said to be in a state of false or metastable equilibrium in contradistinction to the phase complex, which is a system in true or stable equilibrium.

We shall confine our attention in what follows to stable equilibria, and we shall not therefore consider the possible formation of supersaturated solutions.

§ 12. We must now consider the second monovariant system which can exist above the eutectic temperature, namely, the system formed by solution in equilibrium with ice. This system can also exist over a range of temperature, and to a given temperature within that range there will correspond a given value for the composition of the liquid phase. At a temperature slightly above the eutectic temperature, the composition of a solution saturated, or in equilibrium, with ice will have the definite value represented by the point *G*; at a different and higher temperature the definite value represented by the point *K*. All points which represent the compositions of solutions saturated with ice at different temperatures lie on a continuous curve *CGKB*, which diverges from the eutectic point, and is called the polythermal saturation curve of ice. Here again the concentration of water in solutions saturated with ice rises with the temperature, *i.e.*, the saturation curve approaches the side *WT* of the rectangle, which represents pure water. The curve reaches its maximum in the point *B* where it intersects this side. Since the point *B* lies both on the side *WT* and on the saturation curve of ice, it represents pure water in equilibrium with ice, or, in other words, it gives the melting point of ice, and it corresponds therefore with a temperature of 0° C. at a pressure of one atmosphere.

The polythermal saturation curve of ice *CB* extends from the common melting point *C*, of $S +$ Ice, in the binary system $W - S$, to the melting point *B*, of ice, in the unary system *W*. At temperatures below that of *C*, solutions cannot exist, and at temperatures above that of *B*, ice cannot exist, in the system.

A point such as *Y* in Fig. 2 represents a mixture containing more water than does the solution *G* saturated with ice at the same temperature. It represents, therefore, a complex of the solution *G* and ice, which is represented at this temperature by the point *L*. In the same way, a point on the conjugation line *FK* represents a complex of the solution *K* and ice *F*. We may say that any point in the area *BPC*, marked Ice + Solution in Fig. 2, represents a phase complex of ice and a solution the composition of which is given by a point on the saturation curve of ice.

§ 13. Finally, let us consider a mixture the composition of which is represented by the point *Z* in Fig. 2. This mixture does not contain as much salt as does the solution *E*, which is saturated with salt at this temperature. Further, it does not contain as much water as the solution *G*, which is saturated with ice at this temperature. The mixture represented by *Z* is, therefore, an unsaturated solution, and this is clearly the case for every mixture represented by a point in the area *TBCA*. This area is the area of unsaturated solutions.

When the only phase which exists in the condensed binary system is an unsaturated solution, the equilibrium is bivariant. At a given temperature, the composition of the liquid phase may possess a whole range of different values. This is clearly shown by Fig. 2; thus at the temperature of the point *Z*, an unsaturated solution can have any composition between those represented by the points *G* and *E*.

A definite significance has now been assigned to every point within the rectangle *TWST'*, and we will summarise the results which we have obtained.

The point *C* gives the eutectic temperature, and the composition of the eutectic solution. The three phases which are in invariant equilibrium at the eutectic point are represented by the points *P*, *C*, and *Q*. The points *P* and *Q* give the compositions of the two solid phases ice and salt, which are in equilibrium with the eutectic solution *C*, and *PCQ* is therefore the invariant conjugation line. If heat be added to the system in equilibrium at the eutectic temperature, the three phases react according to the following scheme:

$$\text{Ice} + S \rightarrow \text{Solution } C.$$

If heat be abstracted from the system, the opposing phase reaction occurs:

$$\text{Solution } C \rightarrow \text{Ice} + S.$$

At the eutectic temperature, these two phase reactions are said to be in a state of equilibrium, a fact which is expressed by the following notation:

$$\text{Ice} + S \rightleftarrows \text{Solution } C.$$

This notation indicates, not only the fact that the three phases are in equilibrium, but it also indicates the phase reactions which occur when heat is added to, or abstracted from, the system in equilibrium; by a convention, the upper arrow of the equilibrium sign, $\rightleftarrows$, is made to indicate the reaction which occurs when heat is added, the lower arrow that which occurs when heat is withdrawn.

When a phase has been consumed by either of these phase reactions, the system gains a degree of freedom and the equilibrium becomes monovariant. At temperatures below the eutectic temperature, the monovariant system Ice + *S* can therefore exist. This behaviour is represented graphically by the fact that immediately below the invariant conjugation line *PCQ*, we find the area *PQWS*, the points of which represent the monovariant complexes S + Ice. At temperatures above the eutectic temperature, the two monovariant systems S + Solution and Ice + Solution can exist. Accordingly, we find in the graphical representation, immediately above the invariant conjugation line, the area *ACQ*, the points of which represent monovariant complexes of S + Solution, and the area *BCP* the points of which represent monovariant complexes of Ice + Solution. The composition of the liquid phase in these two monovariant systems varies with the temperature, and this variation is represented by *CA*, the saturation curve of the salt, and *CB*, the saturation curve of ice. The saturation curve of ice extends continuously to the melting point of ice, that of the salt to the melting point of the salt, always provided, however, that the monovariant complexes formed by solid salt in contact with saturated solution are stable through the whole temperature range.

If the melting point of the salt is high, it may happen, namely, that before this temperature is reached the salt is decomposed by water, the critical temperature of the mixture is reached, or the liquid phase separates into two immiscible layers. In any of these cases the saturation curve of the salt will not extend continuously to the melting point of the pure salt.

Finally, if on raising the temperature in either of these monovariant systems the solid phase is completely removed (by dissolution), the resulting unsaturated solution is in a state of bivariant equilibrium. These unsaturated solutions, or bivariant phases, are represented graphically by points in the area *TBCAT'*.

We see that the polythermal diagram gives much more than the composition of saturated solutions ; it gives precise information about *any* binary mixture at any temperature ; it tells us whether the given mixture at a given temperature forms an unsaturated solution, a saturated solution, or a phase complex, and in the last case it defines both the nature and the composition of the phases which form the complex. The polythermal saturation curves form a part only of the complete polythermal representation of the binary system. There exists, unfortunately, a tendency to lay all the stress upon the saturation curves, and to ignore the various complex areas of which they form the boundaries, for this reason the mass of information given by a picture such as Fig. 2 is not always appreciated.

Each of the saturation curves *CA* and *CB* can be considered from two points of view. The point *A* represents the temperature at which pure liquid salt and pure solid salt can be in equilibrium, *i.e.*, it gives the melting point of pure solid salt or the freezing point of pure liquid salt. If now a certain small percentage of water be added to the salt, so that the composition of the mixture is represented no longer by the point *S* but by the point *O*, then at the temperature of the melting point of the pure salt this mixture will be completely liquid, since it is represented by the point *A′* (Fig. 2), which lies in the area of unsaturated solutions. On cooling the mixture, it will first deposit solid salt at the temperature of the point *M*, where the unsaturated liquid first becomes saturated. If, by analogy, we call the temperature of the point *M* the freezing point of the mixture, then it is clear that the freezing point has been lowered from *A* to *M* by the addition of a percentage of water measured by *MN*. If a greater percentage of water be added, then the temperature at which the liquid mixture first deposits solid salt is still lower, and may be given by a point such as *D*.

Thus the saturation curve *CA* can be considered as giving the depression of the freezing point of the pure salt as increasing amounts of the second component, water, are added. This is the view which is taken when, of the two variables, temperature and composition, the relations of which are depicted in Fig. 2, the composition is considered as the independent variable; to a given composition there corresponds then a certain freezing point of the liquid mixture.

On the other hand, if, of the two variables, we choose temperature as the independent variable, we may say that, to a given temperature, there corresponds a certain concentration of the salt in the saturated solution, and this concentration is called the solubility of the salt in water at the given temperature. The saturation curve *CA* can, then, also be considered as giving the alteration in the solubility of the salt as the temperature is raised.

In the expression "solubility of a salt in water," a distinction is made between the components of the binary system, whereby one component (water) is considered as the solvent and the other (salt) as the solute; this distinction finds no theoretical justification, however convenient it may be in practice. The concentration of the salt in the saturated binary solution is called the solubility of the salt in water, because at the ordinary temperatures the concentration of the water in the solution is often much greater than that of the salt. We see, however, that the polythermal saturation curve extends continuously from low temperature regions, where the concentration of the water may be comparatively high, to high temperature regions, where the concentration of the water may be exceedingly low; the expression "solubility of a salt in water" is therefore misleading, and by it we must understand the concentration of a salt in its binary saturated solution.

The saturation curve *BC*, of ice, can be considered from the same two points of view. It may be considered either as giving the depression in the freezing point of water as increasing amounts of the second component, salt, are added, or it may be considered as giving the alteration in the solubility of ice as the temperature rises.

It was generally the custom to consider the saturation curve of the salt only as a "solubility" curve, the saturation curve of ice only as a "freezing-point" curve, and it is for this reason that the importance of the complete polythermal picture, with its various complex areas, is often unrecognised. We need make no distinction between solubility curve and freezing-point curve; these are merely the two aspects of the polythermal saturation curve, which gives at all possible temperatures the composition of the liquid phase in a monovariant system.

§ 14. The polythermal relationships represented in Fig. 2 hold strictly for a fixed pressure, and in order to represent the behaviour completely it would be necessary to construct a number of such pictures for different pressures. It is, however, characteristic of the condensed system, where only solid and liquid phases can occur, that variations in pressure, provided they are not too great, have very little effect upon the remaining conditions of equilibrium. Let us, for example, consider the condensed unary system represented by the point *B* in Fig. 2, the system composed of water in equilibrium with ice at its melting point. The temperature corresponding with this point at atmospheric pressure is 0° C.; at 8·1 atmospheres it is – 0·059°, and at 16·8 atmospheres – 0·129°. We see that an increase of 16 atmospheres in the pressure produces an alteration in the equilibrium temperature which is negligible for most purposes. In the majority of cases we may safely assume that an alteration of a few atmospheres in the pressure of a condensed system will effect an alteration in the remaining equilibrium conditions which can be neglected for practical purposes. The same may be said about a system which is not condensed, provided that we consider only the conditions of equilibrium between solid and liquid phases.

The behaviour is very different when a vapour phase is involved in the equilibrium considered. Thus water vapour at a pressure of 4·6 mm. of mercury is in equilibrium with water at 0° at a pressure of 17·4 mm., with water at 20°, and at one atmosphere pressure, with water at 100°. In this case small variations of pressure have considerable effect upon the equilibrium temperature.

Let us consider, as an example, the determination, in practice, of the saturation curve of a salt. Let us suppose that water and the salt are stirred together in an open vessel, and at a certain constant temperature *T*, in such proportions as to insure the presence of excess of solid salt when equilibrium has been established between solid and liquid phases. We will suppose that a sample of the solution is analysed, when this equilibrium has been attained, *i.e.*, when the solution has become saturated with the salt. The result of the analysis would enable us to fix one point on the saturation curve, for it would give us the composition of the solution in equilibrium with solid salt at the chosen temperature *T*. We cannot, however, in this case consider the system as condensed, since a vapour phase is present, and its pressure must be equal to the pressure of the water vapour contained by the atmosphere at the time of the experiment. This pressure will not, in general, be equal to the vapour pressure of the saturated solution, and the three-phase system solid salt–solution–vapour is strictly incapable of stable existence under these conditions. We know that this is so, since if the system is left exposed to the atmosphere for a sufficient time, the liquid will in many cases entirely evaporate, and we shall be left finally with the stable two-phase system solid salt-vapour at the pressure of the water vapour in the atmosphere. In these cases, the vapour pressure of the saturated solution is greater than that of the water vapour contained by the atmosphere, and the system cannot therefore be in a state of equilibrium until the liquid phase has disappeared. In other cases, such as that of the saturated solution of calcium chloride at the ordinary temperature, the vapour pressure is less than the normal pressure of water vapour in the atmosphere, and in these cases water vapour will condense. This will result in a further dissolution of solid salt to maintain the constant composition of the solution, and eventually the solid phase will be entirely consumed by this phase reaction. We shall then be left with the stable two-phase system unsaturated solution–vapour, where the composition of the unsaturated solution is such that its vapour pressure equals the pressure of the water vapour in the atmosphere. Here again, therefore, the three-phase system is not in a true state of equilibrium.

Since, however, at temperatures below the boiling point of the solution the rate at which condensation or evaporation of water occurs is small compared with the rate at which equilibrium is established between solid and liquid phases, we can determine in the way which we have described the composition of the solution in equilibrium with solid salt and vapour at pressures where the system is strictly unstable, *e.g.*, at pressures less than the vapour pressure of the solution.

Let us suppose next that, in a second experiment, excess of solid salt is shaken with solution in a sealed and evacuated tube at the same temperature T as in the previous experiment, and that a sample of the solution is again analysed when equilibrium is established. The pressure must then clearly be equal to the vapour pressure of the saturated solution at this temperature, and the analysis will give us the point on the saturation curve corresponding again with the temperature T, but at a pressure equal to the vapour pressure of the solution in the stable three-phase system.

Finally, let us suppose that in a third experiment, made in an open vessel, the surface of the solution is covered with a layer of an insoluble oil. The oil will prevent the evaporation of water and we can consider the vapour phase as absent, the water vapour contained by the atmosphere being entirely isolated from the system by the layer of oil. The system is then a condensed one under a pressure of one atmosphere, and an analysis of the solution will give the point on the saturation curve corresponding with the temperature T.

In the three experiments described, we have investigated the conditions of equilibrium between the solid salt and its saturated solution first, when the system was under atmospheric pressure, a vapour phase being present the partial pressure of which was less than the vapour pressure of the saturated solution, so that the latter was actually unstable; secondly, when the system was under the pressure of its own vapour, and thirdly, when the system was under atmospheric pressure, the vapour phase being absent. The results of these experiments must, however, be identical, for the effect of such variations in the pressure upon the equilibrium between liquid and solid phases will certainly be smaller than the experimental errors of analysis.

In order to simplify the theory, we shall only consider condensed systems in this book. For the actual application of this theory in practice, we see that this restriction is unnecessary, provided that we consider only the conditions of equilibrium between solid and liquid phases. The practical determination of a polythermal saturation curve such as CA in Fig. 2 is most conveniently carried out in the lower temperature ranges, by stirring excess of the solid salt with solution in an open vessel at a number of known temperatures. An analysis of the solution will give the point on the saturation curve which corresponds with the experimental temperature. This method cannot, however, be used at temperatures near, or above, the boiling point of the solution, since its vapour pressure then becomes equal to, or greater than, that of the atmosphere; the liquid phase, already unstable at lower temperatures, now evaporates too quickly to permit the establishment of equilibrium between salt and solution. In order to follow the saturation curve at higher temperatures, we must work with sealed vessels, under pressures above that of the atmosphere. A series of observations made in this way, first at low temperatures and atmospheric pressure, then at higher temperatures and increasing pressures, may in practice be incorporated in one polythermal diagram although they were made at varying pressures. Provided that the pressure does not become too high, we can assume, with but little error, that the conditions of solid–liquid equilibrium are the same as those which would obtain in a condensed system at truly constant pressure.

Theory predicts that the saturation curve of a salt must extend continuously to the melting point of the salt, provided that it is not decomposed by water at these high temperatures, that the critical temperature of the mixture is not reached, and that two liquid layers are not formed.

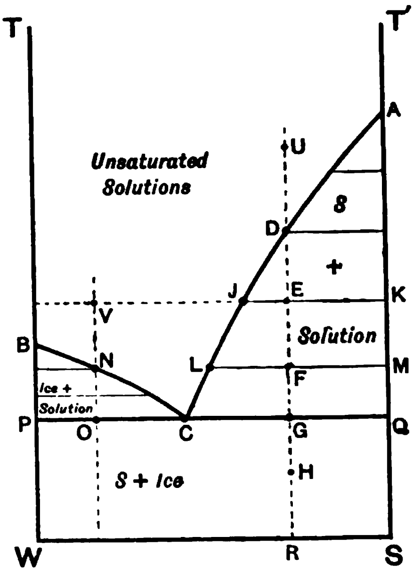

FIG. 3.

The saturation curves of some salts have been determined for the whole temperature range within which saturated solutions are possible, namely, from the eutectic temperature to the melting point of the salt. In the case of salts with a high melting point, a complete investigation offers, however, very great difficulties on account of the high pressures which are generated.

§ 15. The behaviour of a given binary mixture when its temperature or its composition is continuously altered can be accurately described by means of the polythermal diagram. The mixture the composition and temperature of which are represented by the point *U* in Fig. 3 forms an unsaturated solution, since the point *U* lies in the area of unsaturated solutions. If the temperature of the mixture is now gradually lowered, whilst its composition remains constant, the point representing the mixture in Fig. 3 must traverse the line of constant composition *UR* in the direction of falling temperature, *i.e.*, towards *R*. The solution will therefore remain at first unsaturated, while the point which represents it remains in the area of unsaturated solutions, but when the temperature has fallen so far that the mixture is represented by the point *D* on the saturation curve of the salt, it will consist of a solution which is just saturated with the salt. When the temperature is further lowered, the point representing the mixture will enter the complex area *ACQ*, and the mixture will then consist of a complex of the two phases, a saturated solution and solid salt. Thus, immediately the temperature falls below that of *D*, the separation of solid salt will begin, and when the temperature of the mixture is represented, for example, by the point *E*, the mixture will consist of the saturated solution *J* in contact with solid salt represented by *K*; when the temperature of the mixture is represented by the point *F*, the mixture will consist of the saturated solution *L* in contact with solid salt represented by *M*. We see that as the point representing the mixture moves from *D* to *G*, the mixture will consist of solid salt in contact with a solution, and the point representing the composition of this solution will move from *D* to *C*, following the saturation curve. When the mixture is represented by the point *G*, the solution will be represented by the point *C*, and it will be saturated, not only with salt, but also with ice. On the further withdrawal of heat from the mixture, both ice and salt will separate, and the temperature will remain constant until the solution has entirely solidified at constant composition. It is clear that the only way in which the solution *C* can solidify without altering its composition during the process, is by depositing the salt and ice in the same proportion as that in which the components *S* and *W* are contained by it. Thus if the composition of the solution *C* is

$$xS, \ (100 - x) \ W,$$

then on the withdrawal of heat, this solution will deposit both solid salt and ice in the proportion of x parts of the solid salt to $100 - x$ parts of ice.

When the mixture, at the temperature of the point *G*, has entirely solidified to a conglomerate of ice and salt, the temperature can continue to fall, but no further change will be observed. The mixture, from now on, will be represented by a point such as *H*, which lies in the complex area *S* + Ice.

If the composition and the original temperature of the mixture are represented by a point such as *V* in Fig. 3, it is clear that on lowering the temperature the solution will become saturated first with ice at the temperature represented by the point *N*. When the temperature is further lowered, ice will separate and between the temperatures represented by *N* and *O* the mixture will consist of a complex of ice and a solution represented on the saturation curve of ice between *N* and *C*. When the temperature of the mixture is represented by the point *O*, the mixture will consist of ice in contact with the solution *C*, which is saturated not only with ice, but also with salt. The further withdrawal of heat will then result in the complete solidification of the solution at constant temperature and constant composition; when the temperature again falls, the mixture will consist of a solid complex of salt and ice, and no further change will be observed.

We can investigate similarly the behaviour of a mixture when its temperature is kept constant, its composition being continuously altered. Such a continuous change in the composition of the mixture can be realised in practice by allowing water to evaporate slowly at constant temperature. We shall then be admitting the existence of a vapour phase, but, as we have already pointed out (§ 14), the behaviour will be represented with sufficient accuracy by Fig. 3, which holds strictly for a condensed system, since we are considering only the equilibrium between solid and liquid phases. If from the unsaturated solution represented by the point *V* in Fig. 3 water is evaporated at constant temperature, then the point representing the mixture must traverse the constant temperature line *VK* in the direction of increasing salt concentrations, *i.e.*, towards the side *ST′*.

The solution will remain unsaturated until so much water has been evaporated that its composition is represented by the point *J*, when the solution will be just saturated with salt.

On the further evaporation of water, solid salt will separate, and the point representing the composition of the mixture will enter the complex area *ACQ*. It will traverse the conjugation line *JK*, and no further alteration will therefore occur in the composition of the solution, which will remain constant at the value represented by J; while the point representing the composition of the mixture moves from *J* to *K*, the actual weight of the solid salt will continuously increase at the expense of that of the solution *J*, until, when the mixture is represented by the point *K*, all the water originally present has been evaporated, and we are left only with pure solid salt at the temperature of the experiment.

§ 16. We must next consider the case in which the salt may separate from its saturated solution in the form of a hydrate of the general formula $S.m\mathrm{H_2O}$, in which *m* gives the number of molecules of water of crystallisation that combine with one molecule of anhydrous salt. The salt hydrate is a compound of the two components which form the binary system, and it is therefore called a binary compound.

There are now three solid phases which can occur in the system, namely, the salt hydrate, the anhydrous salt, and ice. In the graphical representation of the system three polythermal saturation curves will appear, one representing solutions saturated, or in equilibrium, with the hydrate, one representing solutions saturated, or in equilibrium, with the anhydrous salt, and a third representing solutions saturated, or in equilibrium, with ice. We may say in general that the anhydrous salt will be incapable of existing in stable equilibrium with solutions at sufficiently low temperatures, since it must combine with water to form the hydrate, whilst at sufficiently high temperatures the hydrate will be incapable of existing in the solid state. The saturation curves of the hydrate and of the anhydrous salt must possess different temperature ranges, the former must exist at comparatively low, and the latter at comparatively high, temperatures.

In the system represented by Fig. 4 there occurs, as a solid phase, a salt hydrate which is denoted by *H*. In this figure *BC* is the saturation curve of ice. It extends in the direction of falling temperature, from the point *B*, which represents ice in equilibrium with water at its melting point, to the point *C*, which represents, not now the solution saturated with ice and the anhydrous salt, which is unstable at this low temperature, but the solution saturated with ice and the salt hydrate. The composition of the salt hydrate itself is represented in Fig. 4 by a point *H* on the line *WS* such that the length *WH* gives the percentage of anhydrous salt, and the length *HS* the percentage of water, contained by the hydrate. The line *HT"*, of constant composition, represents therefore the salt hydrate at various temperatures, just as the line *ST'* represents the anhydrous salt at various temperatures.

At the temperature of the invariant point *C*, the three phases, ice, hydrate, and the solution *C*, are in equilibrium. At this temperature the hydrate is represented by the point *Q* and ice by the point *P*, whilst *PCQ* is the invariant conjugation line. If heat be withdrawn from the three-phase system in equilibrium at the invariant temperature, the solution will solidify at constant temperature and constant composition to a solid conglomerate of ice and the hydrate :

$$\text{Solution } C \rightarrow \text{Ice} + H$$

The temperature cannot fall until the solution has entirely disappeared, since all the conditions of the invariant equilibrium are fixed. The temperature of the system invariant point *C* is, therefore, again a lower temperature limit to the existence of the liquid phase ; the point is, in other words, a eutectic point, and all points in the area *PQHW*, which lies below the invariant conjugation line, represent complexes of the two solid phases *H* and Ice.

If heat be added to the system in equilibrium at the eutectic point *C*, the opposing phase reaction will occur :

$$\text{Ice} + H \rightarrow \text{Solution } C.$$

Ice and the hydrate will melt at constant temperature, and in such a way as to keep the composition of the liquid phase constant. The system will gain a degree of freedom and the temperature will rise only when a solid phase has disappeared, leaving one of the monovariant systems :

Ice + Solution
or *H* + Solution,

according to the proportions by weight in which the phases were originally present. Above the invariant conjugation line in the graphical representation, we find therefore the area *BCP*, which is bounded by *BC*, the saturation curve of ice, and the points of which represent monovariant complexes formed by Ice + Solution.

The second monovariant system, *H* + Solution, must be similarly represented by an area lying above the invariant conjugation line and bounded by the corresponding saturation curve of the hydrate. We see, therefore, that the saturation curve of the hydrate diverges from the eutectic point C in the direction of rising temperature ; it will be necessary to consider the form of this curve very carefully, and for this purpose we will approach it from the direction of high temperatures, where the anhydrous salt is the stable solid phase.

The point *A* represents the solid anhydrous salt in equilibrium with the liquid anhydrous salt at the melting temperature, and this point must form, as we have seen in § 11, a temperature maximum in the saturation curve *AD* of the anhydrous salt ; this curve diverges from the point *A* in the direction of falling temperature, and points on it give the compositions of solutions saturated with the anhydrous salt. The solution represented, for example, by *K* is in equilibrium with solid anhydrous salt represented by *L*. If the solution *K* is cooled it will deposit anhydrous salt, and the point representing the composition of the liquid phase in the resulting complex will traverse the saturation curve in the direction of falling temperature. When the temperature has fallen to a certain point, the formation of the salt hydrate will become possible, and we will suppose that at the temperature of the point *D* in Fig. 4, the salt hydrate is formed as a second solid phase. Since three phases (*S*, *H*, and Solution) are now present in the condensed binary system, the equilibrium becomes invariant and the point *D* is therefore a second system invariant point. Solid anhydrous salt and solid hydrate can only be in equilibrium with a solution of the composition represented by *D*, and at the temperature represented by *D*. It follows, therefore, that if heat be withdrawn from this three-phase system, a phase reaction will take place at constant temperature which keeps the composition of the liquid constant. If we wish to determine the nature of this phase reaction we must distinguish the two following cases : the invariant solution *D* may contain a smaller percentage of water than does the hydrate *H*, or it may contain a greater percentage of water than does the hydrate. In Fig. 4 the percentage of water contained by the solution *D* is represented as less than that contained by the hydrate, since the point *D* is nearer to the side *ST′* (which represents pure salt), than is the point H ; we will consider this case first. Let us suppose that a certain small amount of the solid hydrate separates from the solution D. The composition of the solution will be altered by the removal of solid hydrate, since a greater amount of water will be withdrawn in proportion to salt than is contained by the solution D ; the solution will thus become richer in salt. It is clear, therefore, that the composition of the solution can be kept constant at the value represented by D, only if a certain amount of anhydrous salt separates simultaneously with the hydrate.

Now let us consider the second case in which the invariant solution contains a greater amount of water in proportion to the salt than does the hydrate, and let us again suppose that a certain small amount of the hydrate separates as a solid phase. The composition of the solution will be altered, since a smaller amount of water will be removed in proportion to salt than is contained by the solution, and the latter will thus become comparatively richer in water, or, what is the same thing, poorer in salt. The simultaneous separation of anhydrous salt can clearly only accentuate this change in the composition of the solution ; the only way in which this composition can remain unaltered on the separation of solid hydrate is by the simultaneous *dissolution* of anhydrous salt.

We see that the behaviour in the two cases is characteristically different. If the solution D contains a smaller percentage of water than does the salt hydrate, then we can express its composition, instead of in terms of water and the anhydrous salt, in terms of the hydrate and the anhydrous salt which are the solids with which it is in equilibrium. The solution can then retain its constant composition by depositing these two solids in the same proportion in which it contains them. If, on the other hand, the solution D contains a greater percentage of water than does the salt hydrate, then we cannot express its composition in positive terms of the hydrate and the anhydrous salt, the solids with which it is in equilibrium; for, in order to express all the water contained in the solution D as its equivalent of hydrate, we shall need a greater amount of anhydrous salt than is actually present in the solution. In this case the simultaneous separation of both hydrated and anhydrous salt cannot maintain the constant composition of the solution. We must treat these two cases separately.

We suppose, first, that the invariant solution *D*, which is in equilibrium with $H + S$, contains a smaller percentage of water than does the hydrate; the point *D* must then lie as in Fig. 4, between the lines *HT″* and *ST′*. The removal of heat from the system in equilibrium at the invariant point *D* results in the following phase reaction at constant temperature:

$$\text{Solution } D \rightarrow H + S,$$

since, as we have seen, this reaction maintains the constant composition of the liquid phase. On the continued removal of heat, the liquid phase will be completely consumed by the reaction, and until this has occurred the temperature cannot alter. Thus the second system invariant point, since it also forms a lower temperature limit to the existence of the liquid phase, is likewise a eutectic point. At the temperature of the point *D*, solid hydrate is represented by the point *M*, solid anhydrous salt by the point *N*, and the line *MDN* is the invariant conjugation line. Points in the space *MNSH*, which lies below this line, represent phase complexes of solid hydrate and solid anhydrous salt.

The addition of heat to the three-phase system in equilibrium at the eutectic point *D*, will cause the opposing phase reaction to occur:

$$H + S \rightarrow \text{Solution } D,$$

and the system will gain a degree of freedom when one of the solid phases has been consumed by this phase reaction. Accordingly, at temperatures above that of the eutectic point *D*, either of the following monovariant systems may exist:

$$S + \text{Solution}$$
$$\text{or } H + \text{Solution}.$$

We find above the invariant conjugation line *MDN* of Fig. 4 the area *ADN*, corresponding with the monovariant system $S +$ Solution. This area is bounded by the corresponding saturation curve of *S*, and its points represent monovariant complexes formed by the two phases *S* and Solution. The second monovariant system, $H +$ Solution, must similarly be represented by an area lying above the invariant conjugation line, and bounded by the corresponding saturation curve of *H*.

The saturation curve of the hydrate diverges therefore from the eutectic point *D* in the direction of rising temperature, and since we have seen, in the beginning of the paragraph, that it diverges from the eutectic point *C* also in the direction of rising temperature, we conclude that it must pass through a temperature maximum somewhere between the two eutectic points as shown by the curve *CED* in Fig. 4.

The position and significance of this temperature maximum will be made clear by the following considerations. Points on the line *HT″* represent, as we have seen, the salt hydrate at various temperatures, and this line intersects the saturation curve *CED* of the hydrate, in the point *E*. Now since the point *E* lies on the saturation curve, it represents a solution in equilibrium with solid hydrate, but since it lies on the line *HT″*, this solution is of the same composition as the solid hydrate. We may therefore say that the point *E* gives the conditions of equilibrium between solid and liquid hydrate, *i.e.*, it gives the melting point of the hydrate. The temperature maximum in the saturation curve of the hydrate lies at the melting point *E* of the salt hydrate, just as the melting point *A* of the anhydrous salt forms a temperature maximum in the saturation curve of that salt, and the melting point *B* of ice forms a temperature maximum in the saturation curve of ice. The saturation curve of the hydrate diverges from the melting point *E on both sides* in the direction of falling temperature. Points on the branch *ED* represent solutions which are in equilibrium with solid hydrate, and which contain more of the component *S* than does the hydrate itself; points on the branch *EC* represent solutions also in equilibrium with solid hydrate, but containing more of the component *W* than does the hydrate. If we take that point of view which considers the binary saturation curve as giving the depression of the freezing point in a unary system produced by the addition of increasing amounts of a second component (§ 13), then we may say that the freezing point of the hydrate, which is the temperature corresponding with the point *E*, is depressed both by the addition of water and by the addition of salt; the branch *EC* of the saturation curve gives the freezing point depression due to the addition of water, the branch *ED* that due to the addition of salt.

This binary system *W* – *S*, may in fact be considered as built up from two other binary systems of a simpler type. The polythermal diagram (Fig. 4) is divided by the line *HT″* into two parts, and each part represents the conditions of equilibrium in a binary system of the simplest type, such as that depicted in Fig. 2. One of these binary systems is formed by the two components water, *W*, and the hydrate, *H*, and it is represented within the rectangle *TWHT″* of Fig. 4. This binary system *W* – *H*, is of the simplest type since it shows only two saturation curves *BC* and *EC*, which are the saturation curves of the solid components, and one eutectic point *C* where the two solid components are in equilibrium with an invariant solution. The second binary system is formed by the two components hydrate, *H*, and anhydrous salt, *S*; the system *H* – *S* is represented within the rectangle *T″HST′* of Fig. 4. It is also of the simplest type, showing only the saturation curves *ED* of the hydrate and *AD* of the anhydrous salt, and the eutectic point *D* which represents the invariant solution in equilibrium with both these solid components.

The area of monovariant complexes formed by *H* + Solution in the binary system *W* – *S* is thus divided into two parts. A point in the area *ECQ* represents a complex of solid hydrate and a saturated solution which is represented on the branch *EC* of the saturation curve, and which contains proportionately more water than does the salt hydrate, whilst a point in the area *EDM* also represents a complex of solid hydrate with a saturated solution, but the latter is now represented on the branch *ED* of the saturation curve, and it contains proportionately more salt than does the salt hydrate.

The area *TBCEDAT′*, which lies above the saturation curves, is, as before, the area of unsaturated solutions.

We may take this opportunity of illustrating the definition of the term "independent component" which was given in § 3. At the point *E*, both the solid and liquid phases which are in equilibrium have the same composition, namely, that of the hydrate.

The weight of water in either phase is related to the weight of anhydrous salt in that phase by the fact that both these components are present in the same proportion in which they combine to form the hydrate.

If heat be withdrawn from the system in equilibrium at the point *E*, the liquid will deposit solid hydrate without changing its composition, and the temperature will not alter until the liquid has completely solidified. When this has occurred, the temperature will fall and we shall be left with the single phase formed by solid hydrate and represented by a point on the line *HT''* between *H* and *E*. If heat be added to the system, the solid hydrate will melt without changing the composition of the liquid phase, and the temperature will not alter until the solid has completely liquefied. When this has occurred the temperature will rise and we shall be left with the single phase formed by an unsaturated solution of the same composition as the hydrate, and represented by a point on the line *HT''* between *E* and *T''*. We see that every phase which can occur in the condensed system formed by the hydrate alone contains the two components *W* and *S* in unvarying proportion, namely, the proportion in which they are contained by the hydrate; for this particular system these are not, therefore, independent components. The condensed system formed by the hydrate is not a binary but a unary system, as is the system formed by water or that formed by the anhydrous salt. We shall see in the next paragraph that this is by no means the case with every salt hydrate.

When we say that the system formed by the salt hydrate alone is a system of one component only, we do not mean, for example, that the unsaturated liquids represented on the line *HT''* between *E* and *T''*, consist only of the hydrate in the sense of the molecular theory. We are not concerned with the molecular state of the phases, but only with the mathematical expression of their compositions.

§ 17. We will now study the second of the two cases which we were led to distinguish in the previous paragraph. We showed there that when the invariant solution in equilibrium with both anhydrous and hydrated salt contains more water than does the hydrate itself, then simultaneous separation of *H* and of *S* from the solution cannot maintain the constant composition of the latter. If hydrate separates from the solution, the composition can only be kept constant by the simultaneous *dissolution* of anhydrous salt.

This case is represented graphically in Fig. 5. The point D represents again the invariant solution which is in equilibrium, both with the anhydrous and hydrated salt, but since this solution contains now more water than does the hydrate itself, the point D lies between the lines HT'' and WT. Solid hydrate at the temperature of the point D is represented by the point M, and solid anhydrous salt by the point N; the line DMN is therefore the invariant conjugation line. The saturation curves of ice and of the anhydrous salt are given, as before, by BC and AD. If a solution represented by a point on the saturation curve of the anhydrous salt be cooled, then solid anhydrous salt will separate, and the point will traverse the saturation curve in the direction of falling temperature. At the temperature represented by the point D, separation of the solid hydrate begins, and since three phases are now present, the further abstraction of heat will not cause the temperature to fall. It will, on the other hand, cause a phase reaction to take place, which maintains the composition of the liquid constant at the value represented by the point D. This phase reaction consists, as we have seen, in the separation of the hydrate from the solution and the simultaneous dissolution of anhydrous salt; the amount of the solid phase H increases at the expense of both the liquid phase D and the solid phase S, but the compositions of the three phases do not alter. The phase reaction which takes place on the withdrawal of heat from the invariant system in equilibrium at the temperature of the point D is therefore the following:

$$\text{Solution } D + S \rightarrow H \qquad . \quad . \quad . \quad . \qquad \text{(i.)}$$

The system will gain a degree of freedom, and the temperature will begin to fall only when one of the phases, Solution D or S, has been entirely consumed by this reaction. Either of the following monovariant systems can therefore exist at temperatures below that of the system invariant point D:

$$\begin{array}{ll} & \text{Solution } D + H \\ \text{or} & S + H. \end{array}$$

We find, accordingly, below the invariant conjugation line

DMN of Fig. 5, an area which represents monovariant complexes formed by the two phases *H* + Solution and which is bounded by the saturation curve of the hydrate, and an area which represents monovariant complexes formed by the two solid phases *S* + *H*.

It is thus seen that the saturation curve of the hydrate diverges from the invariant point *D* in the direction of falling temperature, and since it diverges from the invariant point *C* in the direction of rising temperature, it extends continuously between the two system invariant points without passing through a temperature maximum; it is represented by the curve *DC* of Fig. 5. This system invariant point *D* differs characteristically from the system invariant point *C*, since below the invariant conjugation line *DMN* there are two complex areas, and one of these represents complexes containing a liquid phase, whilst below the invariant conjugation line *PCQ* there is only one complex area, representing completely solid complexes. Thus the system invariant point *D* is not a lower temperature limit to the existence of the liquid phase; a saturation curve (that of the hydrate) diverges from it in the direction of falling temperature.

The point *D*, unlike the point *C*, is not a eutectic point; it is called a transition point.

We distinguish two types of system invariant points—the eutectic point, which is a lower temperature limit to the existence of the liquid phase, and from which all saturation curves diverge in the direction of rising temperature; and the transition point, which is not a lower temperature limit to the existence of the liquid phase, and from which at least one saturation curve diverges in the direction of falling temperature.

A point such as *F* on the saturation curve of the hydrate is in equilibrium with solid hydrate at the same temperature represented by the point *G*. The line *FG* is a conjugation line and any point on it represents a complex of the two phases solid hydrate and the solution *F*. The area *DCQM*, which is generated by the conjugation line *FG* when the point *F* moves up and down the saturation curve, is therefore the area of monovariant complexes formed by the two phases *H* + Solution. The second complex area which lies below the invariant conjugation line *DMN* is given by *MHSN*, and points in this area represent the completely solid complexes formed by the two phases $H + S$. We can see this more clearly if we consider the behaviour of the mixture represented by the point R, when its temperature is lowered. This mixture has the same composition as the hydrate and at the temperature of the point R it forms an unsaturated solution.

When the temperature is lowered, the solution will first become saturated with anhydrous salt at the temperature represented by the point K. This salt will then separate if the temperature is further lowered, and the point representing the composition of the solution will follow the saturation curve until it reaches the point D, whilst the point representing the mixture will traverse the line KH until it reaches M. The salt hydrate will then begin to separate and the temperature will remain constant while the phase reaction (i) occurs; the solution D will react with the anhydrous salt to form the salt hydrate. Since, now, the two components W and S are present in the mixture M in exactly the right proportion to form the hydrate, without leaving excess of either component, this phase reaction will result in the *simultaneous* disappearance of both phases, solution D and anhydrous salt, and we shall be left with the single phase, solid hydrate. A mixture represented by a point on the invariant conjugation line DMN to the right of M, contains less water than the mixture M, and when the phase reaction (i) occurs, the solution D must therefore disappear before the solid salt S and we shall be left with a solid complex of $H + S$. The area $MHSN$ to the right of the line MH represents, therefore, as we have already said, the monovariant complexes formed by the two solid phases $H + S$. On the other hand, a mixture represented by a point on the invariant conjugation line DMN, to the left of M, contains more water than the mixture M, and the solid salt S must first be consumed by the phase reaction (i); we shall then be left with a monovariant complex formed by the phases $H +$ Solution, and represented by a point in the area $DCQM$.

If heat be added to the system in equilibrium at the transition point, then that phase reaction must occur which is opposed to reaction (i), namely:

$$H \rightarrow \text{Solution } D + S \quad . \quad . \quad . \quad . \quad \text{(ii)}.$$

The system will gain a degree of freedom, and the temperature will rise only when the solid hydrate has disappeared. Above the invariant temperature the only monovariant system which can exist is that formed by the two phases S + Solution.

In agreement with this, we find above the invariant conjugation line DMN, only the area ADN the points of which represent complexes of the anhydrous salt and a solution on the saturation curve AD. If we start with the hydrate at the zero temperature represented by the point H, then on raising the temperature, the hydrate will remain solid until it is represented by the point M, at the transition temperature. At this temperature it will break down according to the phase reaction (ii.) into the solution D and the anhydrous salt. Unlike the case discussed in the previous paragraph, the salt hydrate does not melt to a liquid of the same composition. The saturated solution of the same composition as the hydrate itself is represented by the point K in Fig. 5, and since this point lies on the saturation curve of the anhydrous salt, the solution is in equilibrium with this salt and not with the hydrate; the hydrate is said in this case to possess no stable melting point, since a liquid of the same composition as the hydrate cannot be in equilibrium with solid hydrate. We have seen that on heating the hydrate to the transition temperature two new phases are formed, the solution D and solid anhydrous salt. The compositions of these phases cannot be expressed in terms of the salt hydrate alone, and the condensed system formed by the hydrate is, therefore, in this case, not a unary system; it is evident from Fig. 5 that the binary system $W - S$ cannot be considered as built up from two simpler binary systems, as was the case when the condensed system H formed a unary system.

§ 18. We will summarise the differences which characterise the two binary polythermal types represented in Figs. 4 and 5.

If the conditions of equilibrium are those represented by Fig. 4, the condensed system H is a unary system. The saturation curve of the hydrate passes through a temperature maximum at the melting point of the hydrate, and the binary system $W - S$ can be considered as built up from the two simpler binary systems $W - H$ and $H - S$, in which only the saturation curves of the components appear. Both system invariant points C and D, which occur in the binary system

$W - S$, are eutectic points, and all saturation curves which diverge from them do so in the direction of rising temperature. The phase equilibria existing at these invariant points are represented by the following schemes :

$$\text{Ice} + H \rightleftarrows \text{Solution } C$$

and

$$S + H \rightleftarrows \text{Solution } D.$$

If the conditions of equilibrium are those represented in Fig. 5, the condensed system H is not a unary system. The hydrate does not possess a stable melting point, the saturation curve of the hydrate does not pass through a temperature maximum, and the binary system $W - S$ cannot be considered as built up from two simpler systems. Of the two system invariant points which occur, one is a eutectic point and the other is a transition point. The equilibrium existing at the eutectic point C is represented, as before, by the scheme :

$$\text{Ice} + H \rightleftarrows \text{Solution } C.$$

That existing at the transition point D is represented by the scheme :

$$H \rightleftarrows \text{Solution } D + S.$$

Finally, we may recall the considerations which led us to distinguish these two polythermal types. The phase theory predicts that when two solid phases coexist in equilibrium with a solution in a condensed binary system at constant pressure, then the state of equilibrium is invariant. If heat be added to, or withdrawn from, the system in invariant equilibrium, a reaction occurs among the phases which leads eventually to the disappearance of a phase, but until this phase has disappeared neither the temperature nor the composition of the liquid phase can alter ; an alteration occurs only in the relative amounts of the three phases, the amounts of some phases increasing at the expense of others. The phase reactions which occur at the system invariant point are therefore subject to the condition that they must be such as to keep the composition of the solution constant, and this condition enables us, as we have seen, to determine the nature of these phase reactions. The case is very simple when the only solid phases which occur in the system are the two components, the only invariant solution which occurs in the system being in equilibrium with these two as solid phases. It is clear that, in this case, the only reactions between the three phases which will leave the composition of the solution unaltered consist, first, in the separation of the two solids from the liquid in the same proportion as that in which the components occur in the liquid, and, secondly, in the opposing process, namely, the simultaneous dissolution of the two solids in this same proportion. If the system is of a higher order than the second, the same conclusions are true. The coexistence of more than two solid phases with the solution will then be necessary in order to render the state of equilibrium invariant, but if these solid phases are the components themselves, then the only phase reaction which can maintain the constant composition of the liquid phase consists in the separation of the solid components in the same proportion as that in which they are contained by the liquid, or in the reverse process.

When a compound, such as the salt hydrate, occurs as a solid phase in the binary system, then the case is not quite so simple. We have seen that the phase reactions which maintain the constant composition of the solution in equilibrium with both hydrated and anhydrous salts depend upon the relative amounts of water contained by the invariant solution and the hydrated salt.

Different reactions occur according to whether the composition of the invariant solution can or cannot be expressed in positive terms of the solids with which it is in equilibrium. When a compound occurs as a solid phase in a system of a higher order than the second, the phase reactions which occur at a system invariant point, and therefore also the polythermal type, may depend, in the same way, upon the relations between the compositions of the various phases in equilibrium at the invariant point. In these more complicated cases it is not so easy to distinguish immediately the various types which may occur, as we were able to do in the case of the salt hydrate in the binary system.

We shall describe in a later chapter a graphical method by which the phase reactions occurring at the system invariant point in the binary system, or in a system of a higher order, can be deduced immediately from a knowledge of the compositions of the phases in equilibrium at this point (Chapter V.)

§ 19. We will consider the behaviour of various mixtures when their temperature or composition is continuously changed, in the case where a salt hydrate with a stable melting point appears as a solid phase in the binary system *W* – *S*. The mixture of the composition, and at the temperature, represented by the point *V* (Fig. 6), forms an unsaturated solution, since the point lies in the area of unsaturated solutions. If this solution is cooled, the point which represents it will traverse the line *VZ* from *V* in the direction of *Z*. The solution will therefore remain unsaturated until its temperature is represented by the point *G*, when it will be just saturated with the salt hydrate. When the temperature is further lowered, the point representing the mixture will enter the complex area *H* + Solution. The mixture will then consist of a phase complex of solid hydrate represented by a point on the line *XM* and a saturated solution represented by a point on the saturation curve between *G* and *D*. As the point representing the composition of the mixture moves from *G* to *J*, that representing the composition of the solution will move from *G* to *D* along the saturation curve. When the mixture is represented by the point *J*, the solution will be represented by the point *D*, and it will be just saturated with the anhydrous, as well as with the hydrated salt. On the further withdrawal of heat, the temperature will no longer change, but the solution will solidify completely at constant temperature to a solid complex of salt hydrate and anhydrous salt.

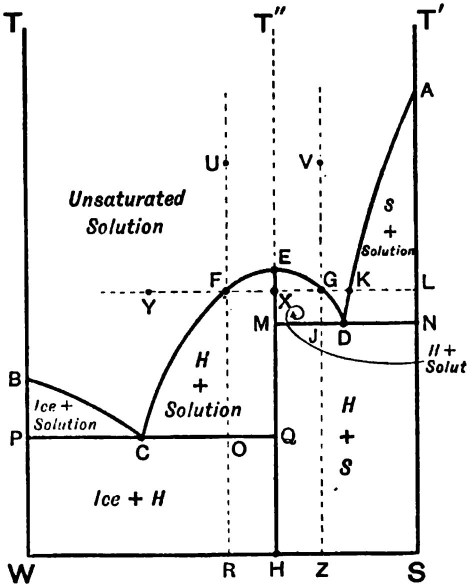

FIG. 6.

The unsaturated solution represented by the point *U* will also become saturated, first with the salt hydrate, when its temperature is lowered. This will occur at the temperature represented by the point F, and when the temperature is still further lowered solid hydrate will separate, and the point representing the composition of the saturated solution will traverse the branch *FC*, of the saturation curve. At the temperature of the point *C*, the solution will become saturated with ice as well as with the hydrate, and it will then solidify at constant temperature and composition to a solid complex of ice and the salt hydrate. We see that for mixtures represented within the rectangle *T″HST′*, the eutectic point *D* gives the lowest temperature at which a liquid phase can exist; at this temperature these mixtures solidify to a phase complex of hydrate and anhydrous salt. For mixtures represented in the rectangle *TWHT″*, the eutectic point *C* gives the lowest temperature at which a liquid phase can exist, and at this temperature mixtures solidify to a phase complex of ice and salt hydrate. We have already seen that solutions represented on the line *HT″* itself solidify at constant composition and at the temperature of the point *E*, to the single solid phase formed by the salt hydrate.

If water is evaporated from the unsaturated solution represented by the point *Y*, the composition of the mixture, as the evaporation proceeds, will be represented by a point which traverses the line *YL* in the direction of the side *ST′*, which represents the pure salt. The solution will therefore become saturated with the salt hydrate at the composition represented by *F*. While the point moves from *F* to *X*, the mixture will consist of a complex of the salt hydrate represented by the point *X* and the saturated solution *F*, which contains proportionately more water than does the hydrate itself.

When so much water has been evaporated that the composition of the mixture is represented by the point *X*, the solution will have dried completely to solid hydrate. On the further evaporation of water, a liquid phase will, however, again appear, and while the point representing the composition of the mixture moves from *X* to *G*, the mixture itself will again form a phase complex, which will now consist of solid hydrate represented by *X* and the saturated solution *G* containing proportionately less water than does the hydrate itself. When the mixture is represented by the point *G*, the solid phase will have again disappeared and the mixture will form a solution which is just saturated with the salt hydrate. On the continued evaporation of water, the point representing the composition of the mixture will enter once more the area of unsaturated solutions between the points *G* and *K*. On the evaporation of water from the solution *G*, which is saturated with the salt hydrate, this solution will actually become unsaturated, and will remain unsaturated until so much water has been evaporated that the composition of the mixture is represented by the point *K*. The solution will then be just saturated with the anhydrous salt, and if more water is evaporated this salt will separate. During the last stage of the evaporation the composition of the solution will remain constant at the value represented by *K*, while anhydrous salt will separate in increasing amount; when finally all the water originally contained by the mixture has been evaporated, we shall be left with solid anhydrous salt represented at the temperature of the experiment by the point *L*.

This remarkable behaviour on the part of the mixture *Y* would be very difficult to explain without the aid of the phase theory. It is seen that the mixture, originally an unsaturated solution, first solidifies completely to the solid hydrate on the removal of water. It then again liquefies, and during a later stage of the evaporation forms once again an unsaturated solution. Finally, it dries completely for a second time, leaving solid anhydrous salt. This behaviour is due to the fact that at the temperature of the mixture *Y* there exist two saturated solutions in the system $W - S$, both in equilibrium with the solid hydrate; this is clearly the case at any temperature which lies between the melting point *E* of the hydrate and the eutectic point *D*. In the monovariant complexes formed by the two phases $H +$ Solution, there corresponds with a given temperature a definite composition of the liquid phase in the binary system formed by the components $W - H$, and a different, but definite, composition of the liquid phase in the binary system formed by the components $H - S$.

We will next suppose that the salt hydrate which occurs as a solid phase in the binary system $W - S$ does not possess a stable melting point. The system is then of the type shown in

Fig. 7, and the system invariant point D is a transition point We have already discussed, in § 17, the behaviour of certain mixtures when the temperature is altered. The unsaturated solution U will become saturated at the temperature represented by K. Anhydrous salt will be deposited, and the point representing the composition of the solution will traverse the saturation curve until it reaches the point D, when the complex itself will be represented by the point G. The salt hydrate will then be formed by the following phase reaction:

$$\text{Solution } D + S \rightarrow H,$$

and neither the temperature nor the composition of the liquid phase will alter during the reaction. Since the point G lies to the right of M, the liquid phase will be completely consumed by this reaction (§ 17), and we shall be left eventually with a solid complex of hydrate and anhydrous salt represented by a point on the line GJ within the corresponding complex area $MHSN$.

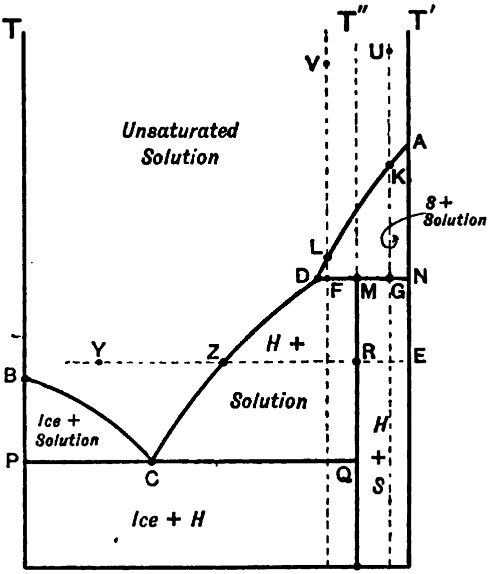

Fig. 7.

An unsaturated solution represented by a point such as V, which lies to the left of the line HT'', will also form a complex of anhydrous salt and the solution D, when its temperature has been lowered to the transition temperature, the mixture being then represented by the point F. In the phase reaction which occurs at constant temperature on the further withdrawal of heat, the anhydrous salt will, however, first be consumed, and we shall be left with the monovariant complex H — Solution, represented by a point in the complex area $DCQM$. The point representing the composition of the solution will therefore traverse the saturation curve DC if the temperature is further lowered, and at the temperature of the eutectic point *C*, the solution will solidify to a complex of ice and the hydrate represented by a point in the complex area *PWHQ*.

If water is evaporated from the unsaturated solution represented by the point *Y*, its composition will alter, being represented by a point which, starting from *Y*, traverses the line *YE* in the direction of the side *ST′*, which represents pure salt.

The solution will therefore become saturated when its composition is represented by the point *Z*. On the continued evaporation of water, the hydrate will be deposited, and the composition of the solution will remain constant at the value represented by *Z* until the liquid phase has disappeared entirely, and there remains only the solid hydrate at the temperature of the experiment, represented by the point *R*. On the further evaporation of water, dehydration of the solid hydrate will begin, and while the point representing the composition of the mixture moves from *R* to *E*, the mixture itself will consist of a solid complex of hydrated and anhydrous salt. When the hydrate has been completely dehydrated, we shall be left finally with the solid anhydrous salt represented by the point *E*.

§ 20. We have so far confined ourselves to the theoretical discussion of heterogeneous equilibrium in condensed systems formed by the two components, water and the salt *S*. A very large number of such systems have been investigated experimentally and the results are to be found in the chemical literature.[1] Since this is not a book of reference, we shall not discuss many of these investigations. It is hoped that the few examples which follow will enable the reader himself to follow the literature on the subject without difficulty.

Very few binary systems composed of water and a salt have been studied at temperatures sufficiently high to give definite information with regard to the upper temperature limit of the salt saturation curve. This is due chiefly to the practical difficulties attached to work at high temperatures and pressures, but partly also to the fact that the earlier experimenters did not realise the continuity of the saturation curve in the high temperature regions. Concerned, as they were, with representing the "solubility of the salt in water," they carried their investigations no higher than the boiling point of the saturated solution at atmospheric pressure.

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[1] Very complete references are given in the tables of Landolt and Börnstein, where many systems are graphically represented.

We have seen that the upper temperature limit of the salt saturation curve is the melting point of the pure salt, provided that the salt is not decomposed by water, that the critical temperature of the mixture is not reached, and that the liquid phase does not separate into two layers. This was first established experimentally by Guthrie,[1] who was also the first to emphasise the arbitrary nature of the distinction between solvent and solute. Guthrie showed that the saturation curve of potassium nitrate in the binary system H_2O-KNO_3, extends continuously to the melting point of pure potassium nitrate. Later, this was shown by Etard[2] to be the case for the binary saturation curves of a number of other salts.

The mathematical form in which the composition of the liquid phase is expressed clearly cannot affect the polythermal type of the system, although it may necessitate some alterations in the graphical representation. We have always expressed the composition of the liquid phase by the weights of each of the components contained in a total of 100 parts by weight of that phase, *i.e.*, in the mathematical form

$$xS,(100-x)W \quad . \quad . \quad . \quad . \quad (1).$$

The composition of the liquid phase is, however, often expressed by the weight of salt which is contained, by the solution, together with a weight of 100 parts of water. The mathematical form is then:

$$yS,100W \quad . \quad . \quad . \quad . \quad (2).$$

It is clear that x and y in forms (1) and (2) are connected by the mathematical identity:

$$\frac{x}{100-x}=\frac{y}{100} \quad \text{or} \quad y=\frac{100x}{100-x}$$

The binary system H_2O-KCl is represented diagrammatically in Fig. 8, the composition of solutions being expressed in the form (2). The only way in which the graphical representation need be changed consists in the measurement along the horizontal concentration axis, of the weight y of salt contained in the solution with 100 parts of water instead of, as before, the weight x contained in 100 weight parts of the total solution. Points on the temperature axis itself represent solutions for which y is zero, *i.e.*, they represent, as before, ice or water at various temperatures. Pure salt, on the other hand, represents a limiting case of the binary mixture for which y, the weight of salt associated with 100 parts of water, is infinitely large. Points representing pure salt are therefore infinitely far removed, and the method of representation possesses this disadvantage, that it is impossible by means of it to show in a finite picture the whole range of binary mixtures from pure water to pure salt. Since, however, the salt saturation curve is seldom investigated at temperatures near the melting point of the salt, this disadvantage is practically unimportant and the method of representation is more generally adopted than that which uses x as the concentration variable; the latter method is, however, better adapted to the theoretical discussion of the binary system.

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[1] *Phil. Mag.* 1884, [v], **18**, 105.

[2] *Ann. Chim. Phys.* 1894, [vii], **2**, 503, abstracted in *Zeitsch. physikal. Chem.*, 1894. **15**, 506.

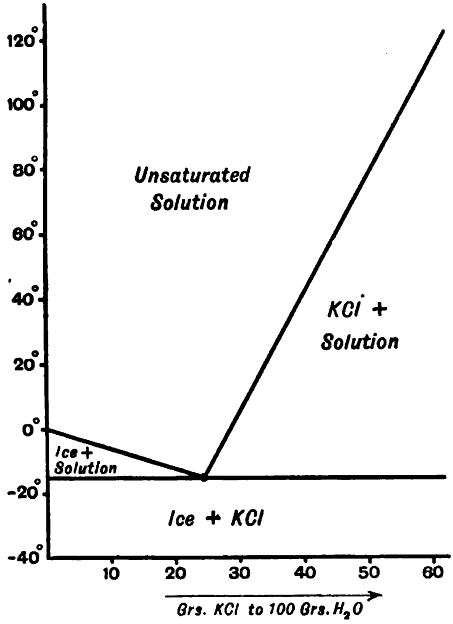

FIG. 8.

The binary system H_2O-KCl is of the simplest type; it can be seen from Fig. 8 that the only saturation curves in the system are those of the components, ice and potassium chloride. The eutectic temperature is −11·1° and the composition of the invariant solution at this temperature,

24·6 grams KCl, 100 grams H_2O.

The boiling point of the saturated solution at atmospheric pressure is 108·5°, so that above this temperature the monovariant system KCl–Solution must be investigated in sealed vessels at pressures above that of the atmosphere. The melting point of pure potassium chloride is 730°, but it was shown by Etard that the saturation curve is probably continuous even to this high temperature. This curve, and the areas of monovariant complexes KCl + Solution and Ice + KCl, extend, therefore, infinitely far to the right of the picture.

The binary system H_2O–NaCl is represented by the same method in Fig. 9. This system differs from the previous one in that a salt hydrate, $NaCl.2H_2O$, appears as a solid phase.

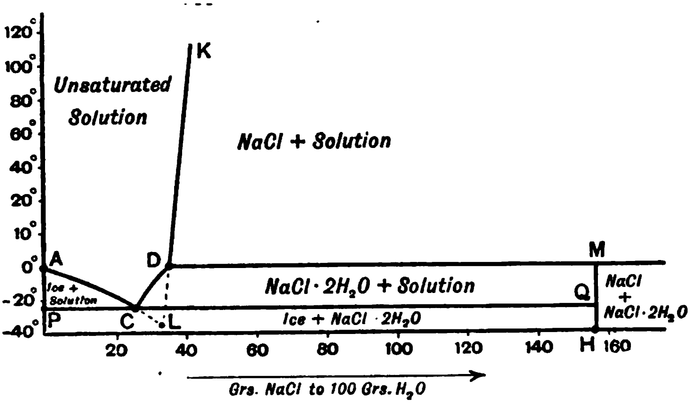

FIG. 9.

AC is the saturation curve of ice, *CD* that of the dihydrate, and *DK* that of the anhydrous salt. The composition of the hydrate $NaCl.2H_2O$, expressed in the form which we are using here, is approximately

162 grams NaCl, 100 grams H_2O.

It is therefore represented at − 40° in the figure by the point *H*, and at various temperatures by points on the line *HM*. The point *D* represents the invariant solution which is in equilibrium with both the hydrate $NaCl.2H_2O$ and the anhydrous salt NaCl. The hydrate is represented at this temperature by the point *M*, the anhydrous salt by a point on the line *DM* infinitely far removed to the right, whilst the line *DM* produced indefinitely to the right is the invariant conjugation line. The composition of the invariant solution *D* is:

35·6 grams NaCl, 100 grams H_2O.

It contains therefore much more water in proportion to salt than does the hydrate itself. The system invariant point *D* is thus a transition point and the corresponding transition temperature is 0·15°. Below this temperature the monovariant system $NaCl.2H_2O$–Solution is stable, above this temperature, the monovariant system NaCl–Solution. The point C gives the temperature and the composition of the eutectic solution which is in equilibrium with Ice + $NaCl.2H_2O$. Ice is represented at the eutectic temperature by the point *P*, the hydrate by the point *Q*, whilst the line *PCQ* is the corresponding invariant conjugation line.

Points in the area *KDM*, which extends infinitely far to the right of the picture, represent the monovariant complexes formed by NaCl + Solution. We pointed out in § 11 that these points may also represent supersaturated solutions. Such bivariant phases are, however, in a state of metastable and not in a state of true equilibrium. They are stable in themselves, but in the presence of a small amount of solid sodium chloride they become unstable, changing to the stable monovariant complexes NaCl + Solution. In the same way, points in the area *DCQM* represent either the stable monovariant complexes $NaCl.2H_2O$ + Solution or the metastable bivariant phases formed by supersaturated solutions. Here, however, there is a third possibility, since these points may also represent the metastable monovariant complexes NaCl + Solution. Such complexes do not form a system in a state of true equilibrium, since in the presence of a small amount of the stable solid phase $NaCl.2H_2O$, they change to the stable complexes $NaCl.2H_2O$ + Solution. If the solid hydrate is rigorously excluded, it is, however, possible to investigate this metastable monovariant system; thus points on the dotted curve *DL* in Fig. 9 represent the compositions of solutions saturated with respect to NaCl, but supersaturated with respect to $NaCl.2H_2O$. The curve *DL* forms a continuous prolongation, in metastable regions, of the saturation curve *KD* of anhydrous sodium chloride. It has been found possible to investigate this curve as far as the eutectic point *L*, where it intersects the metastable prolongation of the ice saturation curve. The point *L* represents the metastable invariant solution in equilibrium with NaCl + Ice, and the corresponding eutectic temperature is lower than that of the stable eutectic point *C* where ice and the hydrate $NaCl.2H_2O$ are in equilibrium with a liquid phase.

The conditions of equilibrium in such metastable monovariant systems can often be determined over a very considerable range of temperature. The binary system $H_2O-Na_2SO_4$ is represented graphically in Fig. 10. The curves in this figure are not drawn accurately to scale, in order that the relations

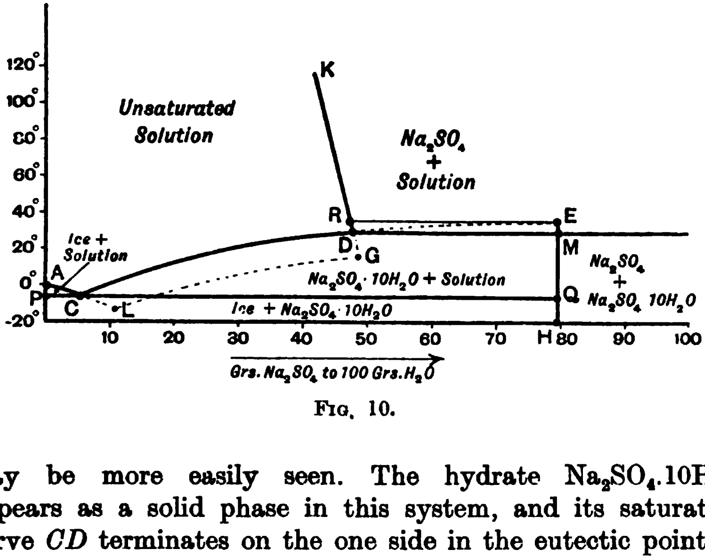

FIG. 10.

may be more easily seen. The hydrate $Na_2SO_4.10H_2O$ appears as a solid phase in this system, and its saturation curve *CD* terminates on the one side in the eutectic point *C*, where the three phases Ice, $Na_2SO_4.10H_2O$, and the solution *C* are in equilibrium, and on the other side in the transition point *D*, where the three phases Na_2SO_4, $Na_2SO_4.10H_2O$, and the solution *D* are in equilibrium; the eutectic temperature is − 1·2°, the transition temperature 32·4°. The decahydrate itself is represented by points on the line *HM*, and since this line does not intersect the saturation curve *CD* in stable regions, the hydrate does not possess a stable melting point. It is, however, possible to follow the metastable prolongation of the saturation curve *CD* as far as the point *E*, where a solution of the same composition as the decahydrate is in (metastable) equilibrium with solid hydrate. The point *E* is the metastable melting point of the decahydrate, and it corresponds with a temperature of 34°. The saturation curve cuts the line *HM* produced in this its maximum point. The point *E* lies in the stable complex area Na_2SO_4 + Solution, and the liquid hydrate is therefore supersaturated with anhydrous sodium sulphate; it will be converted into a phase complex of the solution *R* and the solid anhydrous salt, when a small amount of the latter is added.

A second hydrate may appear as a solid phase in this system, namely, the heptahydrate $Na_2SO_4.7H_2O$, but *no* solution can exist in true equilibrium with this hydrate. The saturation curve of the heptahydrate is given by the dotted line *LG* in Fig. 10, and it can be seen that every point on it represents a metastable solution. For the greater part of its length it lies in the area of stable complexes $Na_2SO_4.10H_2O$ + Solution. In spite of this, it has been found possible to determine the metastable eutectic point *L*, where the saturation curve of the heptahydrate intersects the metastable prolongation of the ice saturation curve, and the metastable transition point *G*, where it intersects the metastable prolongation of the saturation curve of anhydrous sodium sulphate. The temperature of the point *L* is $-3{\cdot}5°$, of the point *G* $24{\cdot}4°$, and both the solutions represented by these points are supersaturated with $Na_2SO_4.10H_2O$.

We shall disregard the possibility of metastable systems in the theoretical considerations of the chapters which follow.

It is to be noticed that the saturation curve *DK* of anhydrous sodium sulphate approaches the side which represents pure water as the temperature rises, and not the side which represents pure salt, as is generally the case. It is therefore probable that this saturation curve does not extend continuously to the melting point of the pure salt, which lies very high on the temperature scale. The discontinuity may be due to either of the three causes already enumerated, namely, decomposition of the salt by water at temperatures below the melting point of the salt, the formation of two liquid layers, or of the critical mixture.

We have so far confined our attention to cases where only one hydrate can exist in stable equilibrium with solutions. The case in which two or more hydrates can so exist does not need particular theoretical consideration. Each hydrate will possess its own saturation curve with the corresponding area of monovariant complexes, and each saturation curve may or may not, pass through a temperature maximum, according to whether the corresponding hydrate does or does not possess a stable melting point. The saturation curve of the hydrate richest in water will have the range of lowest temperatures, the others following in order, as progressive dehydration occurs. The point of intersection of two successive saturation curves will mark a system invariant point, representing the composition of a solution which is in equilibrium with the two solids the saturation curves of which intersect in that point; the system invariant point may be either a eutectic or a transition point.

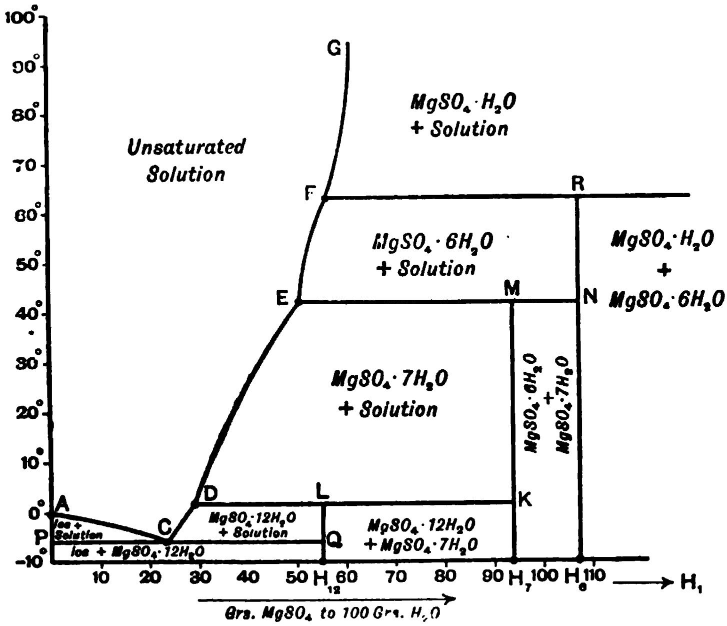

FIG. 11.

The binary system $H_2O-MgSO_4$ is represented diagrammatically in Fig. 11. In this system four different hydrates can exist in stable equilibrium with solutions; these hydrates are $MgSO_4.12H_2O$, $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, $MgSO_4.H_2O$, and their compositions are represented by the points H_{12}, H_7, H_6, H_1, respectively, in Fig. 11.

AC is the saturation curve of ice, *CD* that of the dodecahydrate $MgSO_4.12H_2O$. The point *C* gives the composite of the eutectic solution which is in equilibrium with

$$\text{Ice} + MgSO_4.12H_2O.$$

Ice at the eutectic temperature is represented by the point *P*, the dodecahydrate by the point *Q*. The phase reactions in equilibrium at the eutectic point *C* are expressed by the following notation:

$$\text{Ice} + MgSO_4.12H_2O \rightleftarrows \text{Solution } C.$$

Below the invariant conjugation line *PCQ*, we find, accordingly, the area $PWH_{12}Q$ representing the monovariant complexes Ice + $MgSO_4.12H_2O$. Above this line, we find the area *ACP*, representing the monovariant complexes Ice + Solution, and the area *DCQL*, representing the monovariant complexes $MgSO_4.12H_2O$ + Solution. The hydrate $MgSO_4.12H_2O$ does not possess a stable melting point. The corresponding saturation curve terminates therefore in a transition point *D*, where it intersects the saturation curve *ED* of the heptahydrate $MgSO_4.7H_2O$. The point *D* gives the composition of the solution which is in equilibrium with the two solid hydrates $MgSO_4.12H_2O + MgSO_4.7H_2O$.

At this temperature the dodecahydrate is represented by the point *L*, the heptahydrate by the point *K*. The phase reactions in equilibrium at the transition temperature are given by the following notation:

$$MgSO_4.12H_2O \rightleftarrows MgSO_4.7H_2O + \text{Solution } D.$$

We find, accordingly, below the invariant conjugation line *DLK*, the area *DCQL* already mentioned, the points of which represent the monovariant complexes $MgSO_4.12H_2O$ + Solution, and the area $LH_{12}H_7K$, representing the monovariant complexes $MgSO_4.12H_2O + MgSO_4.7H_2O$. Above the invariant conjugation line, we find the area *EDKM*, representing the monovariant complexes $MgSO_4.7H_2O$ + Solution. The heptahydrate does not possess a stable melting point. Its saturation curve terminates therefore in the transition point *E*, where it intersects the saturation curve of the hexahydrate $MgSO_4.6H_2O$. The point *E* gives the composition of the solution in equilibrium with the two solid hydrates $MgSO_4.7H_2O$, represented by the point *M*, and $MgSO_4.6H_2O$, represented by the point *N*. The phase reactions in equilibrium at this transition point are:

$$MgSO_4.7H_2O \rightleftarrows MgSO_4.6H_2O + \text{Solution } E.$$

Below the invariant conjugation line *EMN*, we find the area *EDKM*, representing the monovariant complexes

$$MgSO_4.7H_2O + \text{Solution},$$

and the area MH_7H_6N, representing the monovariant complexes $MgSO_4.7H_2O + MgSO_4.6H_2O$. Above the line, we find the area *FENR*, representing the monovariant complexes

$$MgSO_4.6H_2O + \text{Solution}.$$

The saturation curve of the hexahydrate also ends in a transition point—the point *F*, where it intersects the saturation curve *GF* of the monohydrate: $MgSO_4.H_2O$. The solution *F* is in equilibrium with the two solid hydrates $MgSO_4.6H_2O$, represented by the point *R*, and $MgSO_4.H_2O$ represented by a point on the line *FR* which is too far removed to be included in Fig. 11. The equilibrium reactions are:

$$MgSO_4.6H_2O \rightleftarrows MgSO_4.H_2O + \text{Solution } F.$$

Below the conjugation line *FR* we find the area *FENR* representing the monovariant complexes $MgSO_4.6H_2O$ + Solution, and an area to the right of the line H_6R, representing the monovariant complexes $MgSO_4.6H_2O + MgSO_4.H_2O$. Above the invariant conjugation line, we find the area *GFR*, representing the monovariant complexes $MgSO_4.H_2O$ + Solution. The upper limit of the saturation curve of the monohydrate is unknown.

It will be clear from this example that the case in which a number of binary compounds can occur as solid phases presents no new theoretical features. All system invariant points with the exception of the point *C* were in this case transition points. As a final example, we choose the system H_2O — $MgCl_2$, which is represented graphically, but only approximately to scale, in Fig. 12. In this system five hydrates appear in stable equilibrium with solutions, namely, $MgCl_2.12H_2O$, $MgCl_2.8H_2O$, $MgCl_2.6H_2O$, $MgCl_2.4H_2O$, $MgCl_2.2H_2O$, represented respectively by the points H_{12}, H_8, H_6, H_4, H_2 in the figure. It can be seen that, of these, the dodecahydrate possesses a stable melting point, given by the point *E*, where the corresponding saturation curve *CD* intersects the line $H_{12}E$. The saturation curve of the hydrate $MgCl_2.12H_2O$ terminates therefore on both sides in a eutectic point and passes through a temperature maximum.

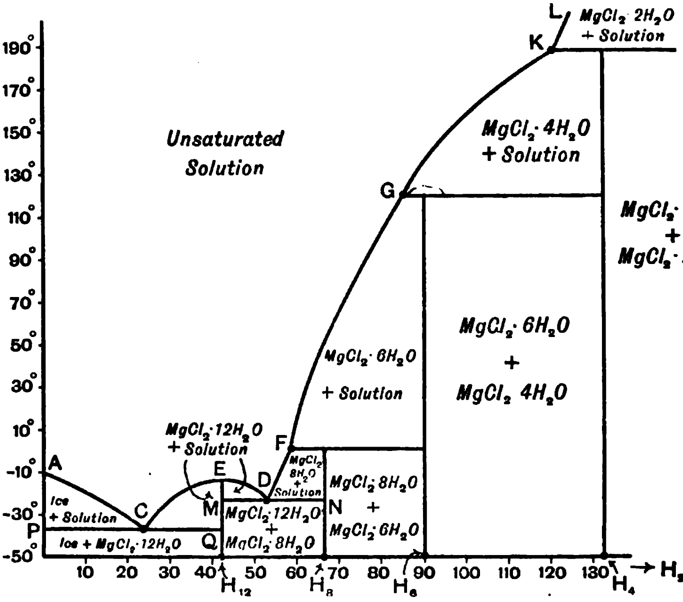

Fig. 12.

The eutectic solution *C* is in equilibrium with Ice + $MgCl_2.12H_2O$.

$$\text{Ice} + MgCl_2.12H_2O \rightleftharpoons \text{Solution } C,$$

and every point below the invariant conjugation line *PCQ* represents a solid complex of these two phases. The eutectic solution D is in equilibrium with $MgSO_4.12H_2O$ + $MgSO_4.8H_2O$.

$$MgSO_4.12H_2O + MgSO_4.8H_2O \rightleftarrows \text{Solution } D$$

and every point below the invariant conjugation line MDN represents a solid complex of these phases. The remaining system invariant points F, G, and K are all transition points; the corresponding equilibrium reactions are:

$$MgCl_2.8H_2O \rightleftarrows MgCl_2.6H_2O + \text{Solution } F.$$
$$MgCl_2.6H_2O \rightleftarrows MgCl_2.4H_2O + \text{Solution } G.$$
$$MgCl_2.4H_2O \rightleftarrows MgCl_2.2H_2O + \text{Solution } K.$$

CHAPTER II

CONDENSED TERNARY SYSTEMS

§ 21. Systems which are formed from water and two salts possessing a common ion present in most cases examples of a three-component system. Such salts can be represented by AC and BC, where the common ion C may be either basic or acidic. We shall again assume that isomorphous mixtures or mixed crystals do not occur, and the liquid phase will then be the only phase of variable composition in the condensed system. The composition of every solid and liquid phase which can occur in the system can be expressed in terms of the three components AC, BC and water, provided that neither salt is decomposed by water. Since, further, the weight of each of these components in the liquid phase can vary independently of the weights of the other two, they form three independent components. The composition of the liquid phase may again be expressed by the weights of each of the components contained in a total of 100 parts by weight of that phase. If, for convenience, we denote two salts by S_1 and S_2 and water by W, then the composition of a given liquid phase will be expressed in the mathematical form :

$$xS_1, yS_2, (100 - \overline{x + y})W.$$

We must then consider as controlling factors of the equilibrium in the condensed ternary system $W - S_1 - S_2$ at constant pressure, the temperature T, the concentration x of the salt S_1, and the concentration y of the salt S_2, in the liquid phase. The third concentration variable—the concentration $100 - \overline{x + y}$ of the water in the liquid phase—is clearly dependent upon the other two. It is actually immaterial which of the three concentration factors we consider as independent variables, the important fact being that there are two such; for convenience therefore we choose x and y.[1]

When we apply the phase rule as a guide to the elucidation of heterogeneous equilibria in this condensed ternary system at constant pressure, we obtain the following results:

1. If four phases coexist, then this system possesses no degrees of freedom. All conditions of equilibrium are perfectly fixed, that is to say, the temperature, and the concentration of each of the components in the liquid phase. This is the case when three solid phases coexist in equilibrium with a liquid phase. As solid phases, we can have the solid salts S_1 and S_2, and if these can neither form a compound with each other, nor a hydrate with water, the only possible third solid phase is ice.

2. If three phases coexist, *e.g.*, two solid phases besides the liquid, the system retains one degree of freedom. It is then necessary to fix the temperature in order to fix the concentrations of the components in the liquid phase. At a given temperature there will be but one solution, of perfectly definite composition, which can remain in equilibrium with the two solid salts S_1 and S_2. We can say that the system S_1–S_2–Solution is in invariant equilibrium at constant temperature and pressure (cf. § 9).

3. If one solid phase only is present in equilibrium with solution the system possesses two degrees of freedom. We may therefore fix the temperature and still retain one degree of freedom; we can say that any one of the systems S_1–Solution, S_2–Solution, or Ice–Solution, is monovariant at constant temperature. Not until we have further fixed one of the two concentration variables, let us say the concentration x of the salt S_1, does the system become completely defined; then the

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[1] Here, again, care must be taken to avoid confusion. The concentration of water is not independent of the concentrations of S_1 and S_2, but water is, nevertheless, an independent component. The actual *weight* of water in a liquid phase of indefinite total weight is in no way dependent upon the weights of S_1 and S_2 in that phase. The *concentration* of water is, however, dependent upon the concentrations of the other two components, since we are here considering a definite weight of the liquid phase, namely, 100 parts. There are three independent components but only two independent concentration variables, just as, in the binary system, there are two independent components but only one independent concentration variable (*cf.* § 3).

concentration y, of the second salt S_2, and therefore also the concentration of water, become likewise fixed.

§ 22. In order to obtain a complete polythermal representation of the system, it will be necessary to show the simultaneous variations of the three factors T, x, and y. A figure of three dimensions is therefore necessary for the complete graphical representation of the condensed ternary system at constant pressure.

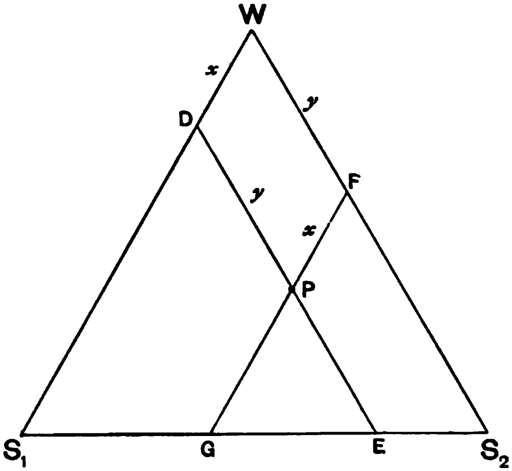

FIG. 13.

The corresponding picture in the binary system was one of two dimensions only, since in this case there was, besides the temperature variable, only one independent concentration variable.

If, however, we fix, not the pressure alone, but also the temperature, then the only two remaining variables are the concentrations x and y of the two salts in the liquid phase. The simultaneous variations of these two at constant temperature can be represented in a plane figure. We shall then begin our investigation of the ternary system by considering the relations which exist at a fixed temperature, between the concentrations of the two salts in the liquid phase. These relations are called the isothermal relations, in contradistinction to the polythermal relations, in which the temperature is a variable. A picture which represents these relations is called an isotherm.

It will always be necessary to state the form in which we express the composition of the liquid phase, since upon this form depends the method of graphical representation to be employed.

Various representations have been used, and although no new experimental facts are revealed by a fresh method, yet the behaviour of the system in any particular respect is greatly illuminated by a proper choice of the method of representation. For the present we shall express the concentration of each component in the liquid phase as a weight percentage of the whole, *i.e.*, we shall use the mathematical form already given :

$$xS_1, yS_2, 100 - \overline{x + y}\, W.$$

A graphical representation is then obtained by means of an equilateral triangle. The equilateral triangle WS_1S_2 (Fig. 13) is chosen so that the length of its side represents 100 per cent., and its vertices the pure components W, S_1 and S_2. The point representing the solution the composition of which is $xS_1, yS_2, (100 - \overline{x + y})W$, is found by means of the following construction :

Assuming that the distance from W to S_1 represents 100 per cent. S_1, we choose a point D on the side WS_1 such that the length WD shall measure x per cent. S_1 on the same scale ; through D a line DE is drawn parallel to the side opposite S_1. In the same way a point F is chosen on the side WS_2, such that the length WF shall measure y per cent. S_2, and through F a line FG is drawn parallel to the side opposite S_2. These two lines intersect in a point P, which represents the phase the composition of which is $xS_1, yS_2, (100 - \overline{x + y})W$. Since the distance WD is clearly equal to PF, it follows that the percentage amount of S_1 contained in a phase represented by a point P inside the triangle is measured by the distance of P from the side opposite to S_1 in a direction parallel to one of the other sides.

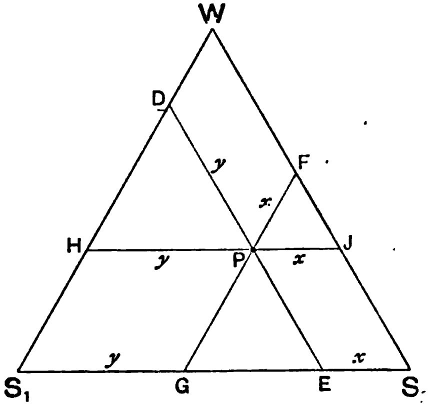

FIG. 14.

Similarly, the percentage amount of S_2 is measured by the distance PD of the point from the side opposite to S_2, also in a direction parallel to one of the other sides. If a third line HJ be drawn through P parallel to the third side S_1S_2 as in Fig. 14, then we shall have three smaller equilateral triangles PFJ, PDH, and PGE inside the triangle of reference. The side of the triangle PFJ measures the percentage, x, of the component S_1, in the phase P. We see, therefore, that we shall obtain the same result whether we measure the amount of S_1 by the distance of P from the side WS_2 parallel either to WS_1 or to S_1S_2. In a similar way, the side of the triangle PHD measures the percentage of S_2 in the phase P.

Now clearly :

$$PJ = ES_2 = x$$

and $$PH = GS_1 = y$$

and since $$ES_2 + GE + GS_1 = 100$$

$$GE = 100 - \overline{x + y}$$

Thus the side of the third triangle PGE measures $100 - \overline{x + y}$ or, in other words, it gives the percentage of the third component—water—in the phase P. We see that this method of graphical representation is symmetrical with respect to each of the three components. A point P inside the triangle represents a ternary mixture in which the percentage amount of *any* component is measured by the distance of P from the side opposite to that component, in a direction parallel to either of the other two sides.

This method of representing ternary mixtures was first used by Gibbs. We see that by means of it we can give actual graphical representation, not only to the two independent concentration variables x and y, but also to the third concentration variable $100 - \overline{x + y}$, which is dependent upon the other two. We are able to do this in virtue of the geometrical property of the equilateral triangle which we have just proved, namely, that the sum of the distances of a point inside the triangle from the three sides of the triangle, measured in directions parallel to the sides, is constant, and equals the length of the side of the triangle. If, therefore, this length is chosen equal to 100, and the distances of the point from two of the sides equal to x and y respectively, then the distance from the third side must equal $100 - \overline{x + y}$.

If the point P in Fig. 15 moves towards the side S_1S_2, it will represent successively a number of ternary mixtures growing continuously poorer in water, since the distance of P

from the side S_1S_2, opposite to W, is continuously decreasing. Finally, when P falls on that side, the water content becomes zero, and the point must therefore represent a binary mixture of S_1 and S_2.

Suppose that its position is now represented by Q (Fig. 15), where QS_2 is equal to a on our scale of measurement, and QS_1 is equal to b or $100 - a$. The point Q denotes a mixture containing a per cent. S_1, since a is the distance of Q from the side opposite to S_1, whilst b, the distance of Q from the side opposite to S_2, gives the percentage amount of S_2 in the mixture. Thus a point Q which lies on the side S_1S_2 of the triangle represents a binary mixture of S_1 and S_2, and the percentage of S_1 in the mixture is given by that section of the line S_1S_2 which lies further from S_1, the percentage of S_2 being given by that section of the line S_1S_2 which lies further from S_2. In the same way, points which lie on the sides WS_1 and WS_2 represent binary mixtures of W and S_1, and W and S_2 respectively, their compositions being similarly measured. We see that binary mixtures may be considered as the limiting cases of ternary mixtures in which the concentration of one of the components has become equal to zero. We see, further, that the composition of a binary mixture of S_1 and S_2, for example, is still given by the lengths of the sections into which the point representing the mixture divides the line S_1S_2, even when the position of the point is referred to the sides of the triangle as in the representation of ternary mixtures. The method which we have used in the previous chapter for representing the compositions of binary mixtures can, therefore, also be considered as the limiting case of the method which is described in this chapter for the representation of ternary mixtures.

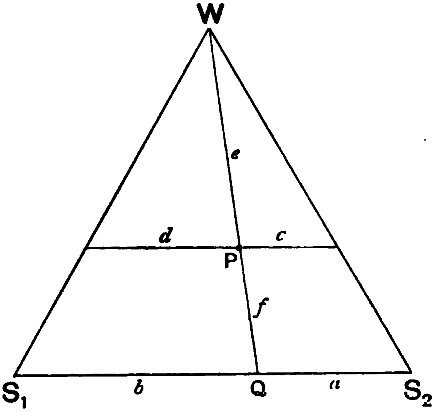

FIG. 15.

Summarising, we can say that all possible mixtures in the ternary system $W-S_1-S_2$ are represented inside the triangle WS_1S_2, or on its periphery if we include the limiting cases where the amount of one or of two of the components must be taken equal to zero ; binary mixtures, namely, are represented on the sides, and pure components at the vertices.

§ 23. We shall now make a few geometrical deductions, using the method of graphical representation which we have just discussed.

Let P (Fig. 15) be any point on the line WQ. The amounts of S_1 and S_2 contained in the ternary mixture P are given respectively by c and d, and the amounts of those components in the binary mixture Q by a and b. Now it is proved in geometry that the ratio c/d is equal to the ratio a/b, and therefore all ternary mixtures represented by points on the line WQ contain the two components S_1 and S_2 in the same proportion a/b. Quite generally, we may say that all points on a line passing through the vertex which denotes one of the pure components represent mixtures containing the other two components in a constant proportion. This result is capable of slightly different expression. The point Q represents a certain mixture containing the two salts S_1 and S_2 in the proportion of a to b ; the addition of water will yield ternary mixtures which will clearly contain the two salts in the same proportion as did the original binary mixture, namely, the proportion a to b. Now we have just shown that mixtures containing S_1 and S_2 in this proportion are represented by points on the line WQ, so we may say that mixtures of the phase or complex represented by Q with water are represented by points on the line joining Q to W. The point Q may here represent one solid phase only, *e.g.*, a compound containing S_1 and S_2 in those proportions, or it may represent, as is generally the case, a mixture of S_1 and S_2, that is, a complex of two solid phases. Similarly, points on the line WQ may represent one phase, *e.g.*, a saturated or an unsaturated solution, or they may represent a complex of a liquid phase with one or two solid phases.

In any of these cases, the above result is always valid—a point on the line WQ represents the total composition of a phase or a phase complex obtained by mixing water with the phase or phase complex represented by Q.

This deduction is only a particular case of a more general

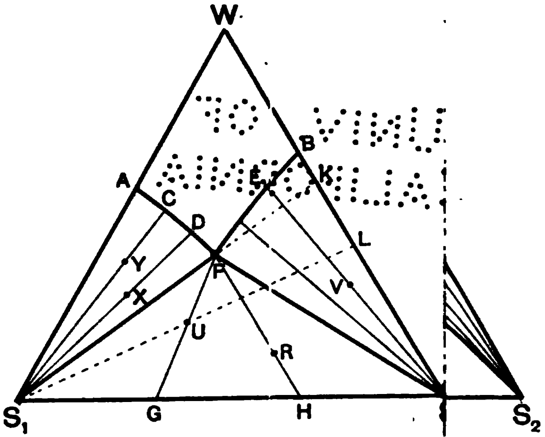

FIG. 16.

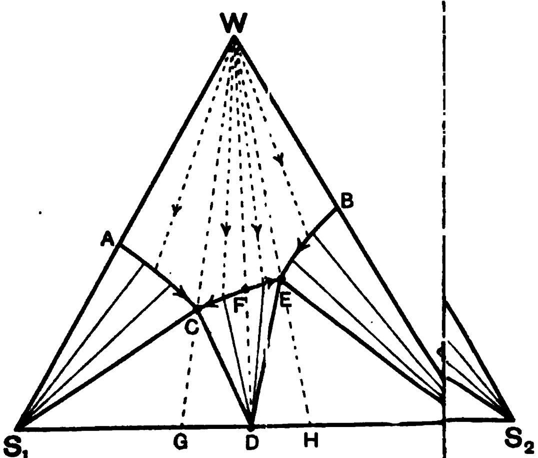

FIG. 20.

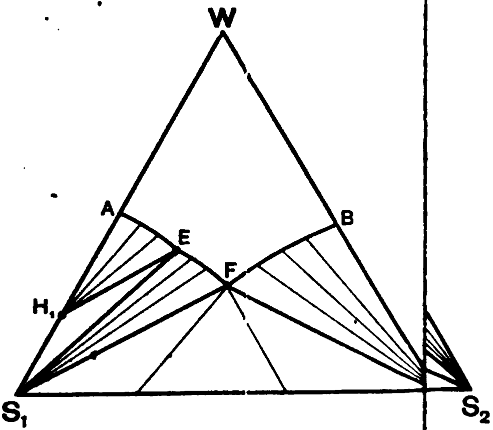

FIG. 23.

23, 24.

geometrical result, which may be stated in the following way. Let any two points in the triangle be taken to represent two different phases or complexes, then mixtures of these two will be represented by points on the straight line joining them. The result holds, therefore, for mixtures of any two complexes or phases in the ternary system, whilst the particular case we have discussed in detail deals with mixtures of a pure component with a binary phase or complex.

[For let us consider any two sides of the triangle as oblique axes of a system of co-ordinates, and let any two points *R* and *S* be defined by the co-ordinates $(x_1\ y_1)$ and $(x_2\ y_2)$. Then x_1 and x_2 represent the percentage amounts of one component in the complexes *R* and *S* respectively, whilst y_1 and y_2 give the percentage amounts of a second component. Any point *P* on the line *RS* has for co-ordinates:

$$\frac{ax_1 + bx_2}{a + b}, \quad \frac{ay_1 + by_2}{a + b},$$

where a and b give the lengths of the sections into which the line *RS* is divided by the point *P*. Now it is seen that $\frac{ax_1 + bx_2}{a + b}$ is the percentage amount of the x component in a complex obtained by mixing a parts of complex *R* with b parts of complex *S*, whilst $\frac{ay_1 + by_2}{a + b}$ gives the percentage of the y component in the same mixture. Thus we arrive at the result stated above: as the point *P* moves along the line *RS* from *S* to *R*, all possible positive values of the ratio a/b are obtained and the point *P* represents successively all possible mixtures of *R* and *S*.]

It thus appears from the geometrical considerations outlined above that if *RS* is a straight line inside the triangle, and *P* a point on it, then *P* represents a phase or complex obtained by mixing the phases or complexes denoted by *R* and *S*; and, further, the mixture must take place in the proportion of the two lengths into which *P* divides the line *RS*.

For example, the point *P* in Fig. 15 represents a phase or complex which results on mixing the binary phase or complex *Q* with water, in the proportion of *e* parts of *Q* to *f* parts of water, where *e* is the length *WP*, and *f* the length *QP*. It should be carefully noticed that the proportionate amount of water in the mixture is given by the length of that section of the line WQ which lies further from W, and the amount of the phase or complex Q by the length of that section which lies further from Q.

The use and value of these geometrical deductions will become clear as we proceed.

§ 24. We will now consider the behaviour of a binary saturated solution of the salt S_1 on the addition of the third component S_2, at a definite temperature t. The composition of the saturated solution of S_1 at this temperature, in the binary system W–S_1, is represented in Fig. 16 by a point such as A on the side WS_1 of the triangle; WA gives the percentage amount of S_1 and S_1A that of water in the binary saturated solution. Suppose now that we have an unsaturated solution formed by dissolving a small amount of the salt S_2 in water, and suppose we saturate this liquid with the salt S_1 by the addition of such a quantity, that excess of the solid salt remains undissolved on the bottom of the containing vessel when equilibrium has been established. The resulting saturated solution will be represented by a point such as C in Fig. 16. The distance of the point C from the side WS_1, opposite to S_2, measures the small concentration of S_2 in the solution, whilst its distance from the side WS_2 measures the concentration of the salt S_1, with which the solution is saturated; this latter concentration will, in general, be different from the concentration of the salt S_1 in the binary solution A, which is also saturated with that salt. Suppose now that a larger proportion of the second salt S_2 is introduced, and the liquid again saturated with S_1. This solution, saturated with S_1, will be represented by another point such as D, which is further than C from the side WS_1, since the solution which it represents contains a greater percentage of S_2 than does the solution represented by C. Proceeding in this way, we obtain a series of points which can be joined by a continuous curve $ACDF$. This curve is characterised by the fact that every point on it represents a ternary solution which is saturated with S_1, *i.e.*, a solution which is in equilibrium with solid S_1. It is, therefore, the ternary saturation curve of S_1, but since every solution which is represented on it is saturated with S_1 only at one and the same temperature t, it must be called an isothermal saturation curve, in contradistinction to the binary saturation curve of S_1 which we discussed in the previous chapter, and which is a polythermal saturation curve. When, however, no possibility of error is present, we shall refer to the isothermal saturation curve more simply as the saturation curve.

Solutions represented by points such as C and D, which lie on the saturation curve of S_1, are in equilibrium with solid S_1 represented by the point S_1. The conjugation lines, which join the points representing the compositions of the two phases in equilibrium, are therefore given by lines such as S_1C and S_1D, which all radiate from the point S_1, and terminate in points on the saturation curve of S_1.

Now by continuously increasing the amount of S_2 contained in solutions saturated with S_1, we shall eventually reach a point F where the solution becomes saturated with the salt S_2 also. This solution F is in equilibrium with both salts S_1 and S_2, since the addition of either cannot further alter its composition. The equilibrium at this point is completely defined since a liquid phase exists here at a fixed temperature in equilibrium with two solid phases (§ 21). There is only one solution which can so exist, and the equilibrium is therefore invariant. This is true, however, only for the fixed temperature t; at any other temperature a different solution will exist in equilibrium with the two solid salts. We must, therefore, define the point F, more strictly, as an isothermal invariant point, in contradistinction to the system invariant point, which marks a definite temperature peculiar to the system. By fixing the temperature we restrict the variability of the system, as was shown in § 9.

The system in equilibrium at the point F is actually monovariant, but since we have fixed the temperature it becomes invariant, or, more strictly, isothermally invariant. When no possibility of error exists, we shall refer to a point such as F simply as the invariant point.

Let us now start from the saturated solution of the salt S_2 in the binary system W–S_2, at the temperature t. The composition of this solution is represented by a point B on the side WS_2 of the triangle, where the length WB gives the percentage of S_2 in the binary saturated solution at this temperature. By the addition of S_1, we obtain a series of solutions, saturated with S_2, and growing increasingly richer in S_1. These solutions are represented by points on a curve *BEF*, which is the (isothermal) saturation curve of S_2, and this curve is characterised by the fact that every solution represented on it is in equilibrium with solid S_2, represented by the point S_2. The conjugation lines radiate, therefore, from the point S_2 and end in points on the saturation curve of S_2.

Clearly the saturation curve of S_2 must also terminate in a point which represents a solution saturated, not only with S_2, but also with S_1, and since there is only one such solution at the temperature *t*, this terminal point must be the invariant point *F*. This point is, therefore, the point of intersection of the two saturation curves; since it lies on both curves, it represents a solution saturated with both salts.

§ 25. We will consider the ternary mixture the composition of which is represented by the point *Y* in Fig. 16; this point lies on the conjugation line S_1C. Now we have shown in § 23 that the composition of a mixture *Y*, represented by a point on the line S_1C, is that of a phase or phase complex which is formed by mixing the two phases represented by the terminal points S_1 and *C*, in the proportion of S_1Y parts of the phase *C* to *YC* parts of the phase S_1. These two phases are, however, in equilibrium with each other, and the point *Y* therefore represents a complex of the two in the above proportion. We see that a point on a conjugation line represents a complex of the two phases denoted by the extremities of the line: this is the same result as that which we obtained for the graphical representation of phase complexes in the binary polytherm.

If a solution, saturated with S_1, grows continuously richer in S_2, then its composition is represented by a point which traverses the saturation curve *AF*, and the corresponding conjugation line sweeps out the triangular area S_1AF. Every point in this area represents, therefore, a monovariant complex of solid S_1 and a saturated solution represented by a point on the curve *AF*. If, for example, the mixture represented by the point *X* is allowed to reach a state of equilibrium at the temperature *t*, it will form the saturated solution *D* in contact with solid S_1 and the proportion by weight in which these two are present will be as the length S_1X is to the length *XD*. Here, again, it must be noticed that the complexes S_1 + Solution are monovariant only at constant temperature, in the same way that the complex $S_1 + S_2 +$ Solution F is invariant only at constant temperature.

Points in the area S_2BF represent the monovariant complexes $S_2 +$ Solution ; the point V, for example, represents a complex of the saturated solution E and solid S_2 in the weight proportion S_2V to VE.

We have shown in § 23 that all points on a line such as S_1F, which passes through the vertex S_1, represent mixtures containing the same proportion of the other two components W and S_2. It is the proportion in which these components are contained by the binary mixture represented by the point K where the line S_1F (produced) intersects the side WS_2 of the triangle.

The proportion is therefore :

WK parts of the salt S_2 to KS_2 parts of water.

It follows, therefore, that the point U of Fig. 16 represents a mixture containing a greater amount of the salt S_2 in proportion to the water than does the solution F, for the proportion is in this case :

WL parts of the salt S_2 to KS_2 parts of water.

In a similar way, by producing S_2F to meet the side WS_1, and joining S_2U, it can be proved that the mixture U contains a greater proportion of the salt S_1 to water than does the solution F, and thence that U represents a phase complex of solid S_1, solid S_2, and the solution F, which is saturated with both. If the straight line FU is produced to meet the side S_1S_2 of the triangle in G, then we have shown in § 23 that a complex of the composition represented by U can be formed by mixing the solution F with the complex represented by G. We have seen, however, that the solution F is in equilibrium with both solid S_1 and solid S_2 in the complex U, and hence the point G gives the composition of this solid mixture. The point U represents, therefore, a phase complex of the solution F with the two solid salts S_1 and S_2, the latter in the proportion of S_2G to GS_1.[1]

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[1] We defined the conjugation line in § 10 as the line joining two points which represent the compositions of two phases in equilibrium with each other. We may describe a line such as FG of Fig. 16 as a conjugation line if we slightly modify the definition; this line joins two points which represent the compositions, not of two phases, but of a phase and a phase complex which are in equilibrium with each other, and it is then still true, as we have shown above, that a point on a conjugation line represents a complex of the phases (now more than two) represented by the terminal points of the line.

Similar conclusions may be drawn with respect to the meaning of every point in the area S_1FS_2. The point R represents a complex of the saturated solution F and the two salts S_1 and S_2, the latter in the proportion of S_2H to HS_1.

We have now found the significance of the three areas S_1AF, S_2BF, and S_1FS_2. Points in the area S_1AF represent complexes of the same solid phase S_1 with various solutions represented on the curve AF, all saturated with this salt. Points in the area S_2BF represent complexes of the same solid phase S_2 with various solutions represented on the curve BF, all saturated with S_2. Points in the area S_1FS_2 represent complexes of the same saturated solution F with varying mixtures of the two solids S_1 and S_2. In order to complete the triangle there remains only the area $WAFB$. It is clear that all mixtures represented in this area contain less of the salts than is necessary to form a saturated solution and hence that this is the area of unsaturated solutions.

We can now see the importance which attaches to the geometrical representation. Fig. 16 gives much more than the composition of saturated solutions at the temperature t. It yields exact information about any possible ternary mixture of water, S_1 and S_2 at the temperature considered. According to whether the mixture is represented by a point on one of the saturation curves, or in one of the various areas, it will form a saturated solution, an unsaturated solution, or a phase complex with one or two solid phases in contact with liquid.

The phase theory yields no information as to the exact form of the saturation curves and complex areas. These are determined by the laws governing the homogeneous equilibria which obtain within the various phases. The phase theory asserts, merely, that, so long as the same solid phase is present, the solutions in equilibrium with it will be represented by points which all lie on one continuous curve, the saturation curve; a discontinuity or breakpoint in the curve indicates a change in the nature of the solid phase.

Summarising, we find represented in Fig. 16:

The area $WAFB$ representing unsaturated solutions at the temperature t.

The area S_1AF representing monovariant complexes S_1 + Solution, at the temperature t; and the saturation curve AF

giving the compositions of the corresponding saturated solutions.

The area S_2BF representing monovariant complexes S_2 + Solution, at the temperature t; and the saturation curve FB giving the compositions of the corresponding saturated solutions.

The area S_1FS_2 representing invariant complexes $S_1 + S_2 +$ Solution, at the temperature t; and the invariant point F giving the composition of the corresponding invariant solution. F

§ 26. We shall consider next the behaviour of ternary mixtures when water is withdrawn from them at constant temperature. The mixture represented by the point C (Fig. 17), which lies in the area $WAFB$, forms an unsaturated solution at the temperature t. If water is isothermally withdrawn from it, for example, by evaporation,[1] the proportion between the concentrations of the two salts will remain unaltered, but the mixture will grow progressively poorer in water. Its composition will therefore be represented by a point which traverses the straight line WE in the direction of E.

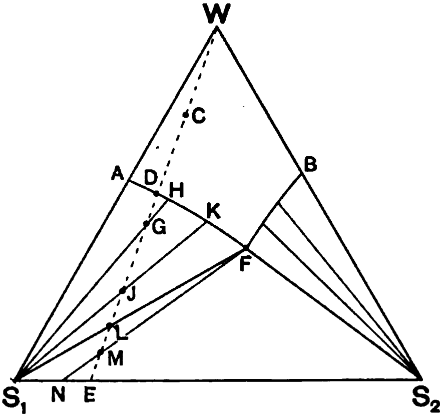

FIG. 17.

At first the point representing the mixture will remain in the area $WAFB$ and the solution will therefore remain unsaturated. This condition will hold until the mixture has lost so much water that its composition is denoted by the point D on the saturation curve of S_1. At this point the solution will be just saturated with the salt S_1, and if still more water is evaporated, the point representing the total composition of the mixture will fall inside the area S_1AF. The mixture will then consist of a complex of the solid salt S_1 and a saturated solution represented by a point on the curve AF. If, for example, the mixture is represented by G, it will form a complex of the saturated solution H and the solid salt S_1. In other words, as soon as more water has been evaporated than corresponds with the point D, separation of the salt S_1 will begin, and the point representing the composition of the solution will move along the curve AF in the direction of F. When the composition of the mixture is given by J, that of the solution will be given by K, and when the composition of the mixture corresponds with the point L, the solution will be represented by the point F and will, therefore, be just saturated with the salt S_2 also. Further evaporation of water brings the point representing the total composition of the mixture within the area S_1FS_2, and solid S_2 must therefore begin to separate together with S_1, whilst the solution retains the constant composition F. Thus, when the water content of the mixture is represented by the point M, a solid complex of the composition represented by N will be in equilibrium with the solution F. As the mixture approaches complete dryness, so the proportion of the two solid salts will approach the value represented by E, until, when all the water has been evaporated, there will remain a mixture of the dry salts S_1 and S_2 in the proportion of S_1E parts of S_2 to ES_2 parts of S_1. During the whole of this time, from the first appearance of S_2 till the final disappearance of the liquid phase, the solution will retain the constant composition F. F is therefore said to be a "drying-up" point.

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[1] Figs. 16 and 17 hold strictly for a condensed system at constant pressure but this restriction need not be made in practice, provided we consider only the conditions of equilibrium between solid and liquid phases (§ 14).

The same phenomena will be observed in the reverse order when water is added in increasing quantity, to the dry salt mixture E at the temperature t.

The behaviour of an unsaturated solution such as that represented by P will clearly be somewhat different (Fig. 18). This solution, on evaporation of water, will remain unsaturated, and the point representing its composition will move along the line WQ until it reaches T. Here the solution will be saturated with S_2 and this salt will commence to separate, whilst the point representing the composition of the solution will move from T in the direction of F along the saturation curve of S_2. As more of S_2 separates, so the composition of the solution will approach more closely to that represented by F, until finally, when this point is reached, the solution will be saturated with both S_1 and S_2, and there will begin separation of S_1 together with S_2. The solution will now no longer change in composition. Both salts will separate and the solid mixture will grow increasingly richer in S_1. The point representing the total composition of the solids, which is given by the point S_2 before the separation of S_1 begins, will traverse the line S_2Q, and a dry mixture of the composition Q will be finally obtained. The composition of the solution during this last stage of the evaporation will remain constant at the value represented by F, and this point is, therefore, again the drying-up point.

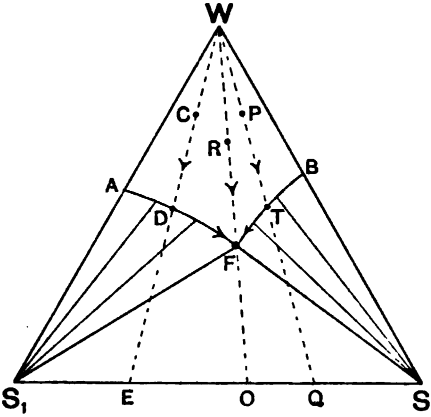


Fig. 18.

The behaviour of an unsaturated solution such as that which is represented by the point R on the line WF, is peculiar. On evaporating water from such a solution, it will remain unsaturated until it attains the composition represented by F, when it will become saturated with both salts simultaneously, and on the further withdrawal of water, both salts will separate. The composition of the salt mixture which is thus deposited is given by the point O, and this mixture contains the two salts in the same proportion as does the solution F which is in equilibrium with them.

As the evaporation of water proceeds, the point representing the composition of the complex moves along the line FO, from F towards O, and therefore from the first appearance of solid at F to the total disappearance of liquid at O, the solution possesses the same invariant composition represented by F, and the solid mixture of S_1 and S_2 which separates retains at every stage the same total composition O, the salts being contained in this mixture in the same proportion as they exist in the solution F. The total composition of the solid which is deposited is the same as that of the solid which remains in solution, and the solution itself retains a constant composition.

A close analogy is thus seen to exist between the isothermal evaporation of the ternary invariant solution and that of the saturated solution of a pure salt. This arises from the fact that a ternary complex in which two solid phases are in contact with solution, and a binary complex in which one solid is in contact with solution, both constitute systems with only one degree of freedom.

The path traversed by a point which represents, in its successive positions, the varying composition of a solution when water is evaporated from it at constant temperature is called the isothermal path of crystallisation of that solution, and it terminates in the drying-up point. The paths of crystallisation in Fig. 18 are indicated by the arrows, and all solutions have the same drying-up point F.

§ 27. We will now assume that two of the components can unite to form a compound. If the two reacting components are the two salts S_1 and S_2, the resulting compound is a double salt of the general formula $nS_1 \cdot mS_2$ where n and m are whole numbers giving the molecular proportions in which the two salts combine. We shall denote the double salt more shortly by D, and it will be represented by the point D (Fig. 19) on the side S_1S_2 of the triangle, the lengths S_2D and DS_1 giving the percentage amounts of the simple salts S_1 and S_2 contained in the double salt.

We shall start, as before, from solutions saturated, or in equilibrium, with solid S_1. In the binary system, where no S_2 is present, the solution saturated with S_1 is represented by the point A. On adding increasing amounts of S_2 to this solution, still in equilibrium with solid S_1, the point representing the composition of the solution will describe the saturation curve AC of S_1. Ultimately, a point C will be reached, at which no more of the salt S_2 will dissolve, but this salt will not now remain unaltered as a solid on the bottom of the reaction vessel, as it did in the case of the system where no double salt was formed. If, to the solution C in contact with excess of solid S_1, a further quantity of the second salt is added, the whole of this added salt will combine with a definite amount of the solid salt S_1, namely, with the amount necessary to form the double salt, and this will result in the appearance of the double salt D as a new solid phase.

Two solid phases—the simple salt S_1 and the double salt D—are now present in equilibrium with the solution, provided that the salt S_2 has not been added in sufficient quantity to convert the whole of the existing solid salt S_1 into the double salt.

The point C represents a solution saturated with both S_1 and D; it is accordingly an invariant point. The composition of the liquid phase will not alter on the addition of more S_2; the latter will merely react to form more double salt at the expense of the existing S_1. The invariant composition will be maintained until sufficient S_2 has been added to convert the whole of the S_1 present as a solid phase into the double salt, but when this has been done the system will regain a degree of freedom, since one phase, the solid phase S_1, will have disappeared. Accordingly, on the continued addition of S_2, the composition of the liquid will again continuously alter as indicated by the curve CE. The solid phase which is in equilibrium with liquids represented on this curve is the double salt D. It is, therefore, the saturation curve of the double salt, and all points on it may be joined by conjugation lines to the point D, which represents the solid phase in equilibrium with these solutions.

A similar behaviour is observed when the salt S_1 is added in increasing amounts to solutions in equilibrium with solid S_2. The saturated solution of S_2, in the binary system W–S_2, is represented by the point B on the side WS_2 of the triangle, whilst points on the saturation curve BE give the compositions of ternary solutions which are also in equilibrium with solid S_2. When the composition of the solution is represented by the point E, the addition of solid S_1 is no longer accompanied by a change in the composition of the liquid phase. This salt does not, however, remain unchanged as a second solid phase, but it combines with an equivalent amount of the solid S_2 which is present, to form double salt as a new solid phase.

The point E represents, therefore, a solution saturated with both the double salt and the simple salt S_2, and it is a second invariant point.

By the continued addition of S_1 to the solution E in contact with solid S_2, we shall eventually convert the whole excess of solid S_2 into the double salt. Until this has been effected the solution will not vary in composition, but as soon as the solid phase S_2 has disappeared, the further addition of S_1 will produce alterations in the composition of the liquid phase, and since the single solid phase now present is the double salt, the composition of liquids in equilibrium with it must be represented by points on the saturation curve CE of the double salt. The two invariant points C and E are thus seen to be joined by a continuous saturation curve, that of the double salt. Fig. 19, which represents the isothermal behaviour of the system $W - S_1 - S_2$ in this case, contains, therefore three saturation curves (each curve representing solutions saturated with one solid) and two saturation points (each point representing a solution saturated with two solids), besides the various complex areas.

The area $WACEB$ represents unsaturated solutions, at the temperature t.

The area S_1AC represents monovariant complexes S_1 + Solution, at the temperature t; and the saturation curve AC gives the compositions of the corresponding saturated solutions.

The area DCE represents monovariant complexes D + Solution, at the temperature t; and the saturation curve CE gives the compositions of the corresponding saturated solutions.

The area S_2BE represents monovariant complexes S_2 + Solution, at the temperature t; and the saturation curve BE gives the compositions of the corresponding saturated solutions.

The area S_1CD represents invariant complexes $S_1 + D$ + Solution, at the temperature t; and the invariant point C gives the composition of the corresponding invariant solution.

The area S_2ED represents invariant complexes $S_2 + D$ + Solution, at the temperature t; and the invariant point E gives the composition of the corresponding invariant solution.

§ 28. Cases frequently arise in which two simple salts may form more than one double salt, the two former being present in different molecular proportions in the various double salts. The isotherms naturally become more complicated in such cases, but they may still be easily deduced by similar methods to those which we have employed. Every new solid phase must possess its own continuous saturation curve, and these curves will follow one another in order between the saturation curves of the simple salts. A change in the solid phase will always result in a discontinuity or break point, and this point will denote an isothermal invariant solution which is in equilibrium with the two solids on the saturation curves of which it lies.

It may be well to emphasise again the limits in the scope of the phase theory. The phase theory defines the conditions of heterogeneous equilibrium, that is to say, the conditions of equilibrium between the various phases of a system. Unless therefore the double salt is capable of existing as a distinct phase, that is to say, unless it is capable of existence in the solid state, it must be considered as non-existent for our present purposes. The actual state in which the two simple salts exist in the solution is immaterial to the phase theory. They may be dissociated into ions or they may be associated as double salt molecules. Upon factors such as these will depend the shape of the saturation curves, but the type of the isotherm (that of Fig. 16 or that of Fig. 19) depends only upon the number of phases which are capable of separate existence.

§ 29. We shall now consider the behaviour of mixtures on the isothermal addition or removal of water, exactly as we did for the case of the simpler system in which no double salt occurred. An unsaturated solution which is formed by dissolving the pure double salt in water will contain the two simple salts in the same proportion as they are contained by the double salt itself. This solution will therefore be represented by a point which lies on line *WD* and in the area *WACEB* (Fig. 20). If water is evaporated from the solution, its composition will be represented by a point which traverses the line *WD* in the direction of *D*. The solution will remain unsaturated until so much water has been evaporated that its composition is represented by the point *F*. This point lies on the saturation curve of the double salt, and the solution at this stage of the evaporation will, therefore, be just saturated with the double salt. The continued removal of water will now result in the separation of the solid double salt, and the formation of complexes represented on the conjugation line *FD*. The composition of the solution will, therefore, no longer alter during the subsequent evaporation of water. As the point which represents the complex moves from F to D, solid double salt will be deposited in increasing amount at the expense of the solution F until, when all the water has been evaporated, the dry solid double salt, represented by the point D, will alone remain.

An examination of Fig. 20 shows that the system W–S_1–S_2 can, in this case, be considered as built up from two simpler systems the components of which are respectively, W–S_1–D and W–S_2–D. The system $W-S_1-D$ is of the simplest type, and it is represented, at the temperature t, within the triangle WS_1D, which we can consider, if we choose, as a new triangle of reference. There occur in this system only the two saturation curves AC and FC of the components S_1 and D, and one invariant point C, which represents the solution saturated with both these components. In the same way the system W-S_2-D is represented within the triangle WS_2D. It shows only the two saturation curves BE and FE, of the components S_2 and D, and one invariant point E which represents the solution saturated with $S_2 + D$.

It therefore follows that the composition of any mixture which is represented by a point within the triangle WS_1S_2 can be expressed in two ways. If the point lies to the left of the line WD, it represents a mixture the composition of which can be expressed either in terms of the components W,S_1, and S_2, *i e.*, by reference to the triangle WS_1S_2, or in terms of water and the two salts D and S_1, *i.e.*, by reference to the triangle WS_1D.

In the same way, the composition of a solution represented by a point which lies to the right of the line WD can be expressed either in terms of W,S_1, and S_2, or in terms of W, S_2, and D. If an unsaturated solution is represented by a point in the triangle WS_1D, then on the isothermal evaporation of water, a saturated solution will be obtained the composition of which is given by a point on one of the curves AC or FC, and in either case the solution will eventually dry at the constant composition represented by the invariant point C. The paths of crystallisation of all solutions which are represented by points in the triangle WS_1D, and which can therefore be formed by mixing the simple salt S_1 and the double salt D with water, end in the drying-up point C. If, on the other hand, the unsaturated solution is represented by a point in the triangle WS_2D, it will first become saturated when its composition is represented by a point on one of the curves *BE* or *FE*, and it will dry at the constant composition represented by the invariant point *E*. Thus the paths of crystallisation of solutions which can be formed by mixing the simple salt S_2 and the double salt with water end in the drying-up point *E*. The paths of crystallisation on the saturation curves are indicated in Fig. 20 by the arrow heads, and these converge, in the triangle WS_1D, on the drying-up point *C*, and in the triangle WS_2D, on the drying-up point *E*.

We have seen that unsaturated solutions which are represented by points on the line *WF*, *i.e.*, which contain the two simple salts in the same proportion as does the double salt, dry at the constant composition represented by the point *F*, and this point is, therefore, a third drying-up point. Mixtures which can be formed from water and the double salt alone may consist of unsaturated solutions represented by points between *W* and *F*, and containing the two simple salts in the same proportion as does the double salt itself; or they may form phase complexes represented by points between *F* and *D*, which contain the saturated solution *F* in contact with solid double salt. In either of these cases the compositions of all phases can be expressed in terms of water and the double salt alone. The system formed by water and the double salt, *at the temperature t*, is, therefore, a binary system. It is true that the compositions of all phases in the system *W–D* at the temperature *t* can also be expressed in terms of the three components *W*, S_1 and S_2, but since the weight of S_1 is related to the weight of S_2, in any phase, by the fact that both salts are present in the same proportion as that in which they are contained by the double salt, these three components are not independent. The point *F* must, therefore, be considered as giving the composition of the saturated solution in the binary system *W–D* at the temperature *t*, in the same way that the point *A* gives the composition of the saturated solution in the binary system $W–S_1$, and the point *B* that of the saturated solution in the binary system $W–S_2$ at the temperature *t*. For this reason, namely, that a particular section of the ternary isotherm represents a system of the next lower order, we are able, as we have already seen, to consider the ternary system $W–S_1–S_2$ at the temperature *t*, as built up from two simpler ternary systems. This case is comparable with that of the binary system in which a salt hydrate occurs with a stable melting point; we saw in § 16 that a section of the polythermal diagram represented a system of the next lower order (a unary system), and we were then able to consider the binary system as built up from two simpler systems.

We have seen that the composition of the invariant solution C can be expressed, by reference to the triangle WS_1D, in terms of water and the two salts S_1 and D with which it is in equilibrium. If water is evaporated from an unsaturated solution represented by a point on the line WG, the solution will become saturated simultaneously with the two salts S_1 and D when its composition is represented by the point C. The solution will then maintain this composition while the two salts separate together in the proportion represented by the point G. The composition of the solid complex G can also be expressed in two ways, namely, in terms of S_1 and S_2 by reference to the line S_1S_2, or in terms of S_1 and D by reference to the line S_1D. Thus, the complex G consists of the two salts S_1 and D in the proportion of S_1G parts of D to GD parts of S_1, and since the line GC passes through the vertex W, this is the same proportion as that in which the salts S_1 and D are contained by the solution G. The invariant solution C maintains, therefore, its constant composition on the evaporation of water, by depositing the two salts with which it is in equilibrium in the same proportion as that in which it contains them.

The composition of the invariant solution E can similarly be expressed, by reference to the triangle WS_2D, in terms of water and the two salts S_2 and D with which it is in equilibrium. It will maintain its constant composition on the evaporation of water by depositing these salts in the proportion in which they are contained by it, namely, in the proportion: DH parts of S_2 to HS_2 parts of D.

§ 30. We have assumed in the previous discussion that the line joining W to D cuts the saturation curve of the double salt. This is by no means necessarily the case, and relationships similar to those depicted in Fig. 21 frequently occur. These call for detailed consideration, since the results arising from them appear at first sight somewhat remarkable. In the case depicted in Fig. 21, exactly as in Fig. 20, AC is the saturation curve of S_1, CE and EB those of D and S_2 respectively; the point C represents the invariant solution in equilibrium with the two solids S_1 and D, and the point E the invariant solution in equilibrium with D and S_2. Here, however, the straight line WD cuts the saturation curve of S_1, instead of that of the double salt, as was the case of Fig. 20. We shall again consider, first, the behaviour of an unsaturated solution which contains the simple salts in the same proportion as does the double salt when water is evaporated from it. Such a solution can be formed by dissolving the pure double salt in water, and it will be represented by a point U on the line WD between W and F. This solution will become saturated when so much water has been evaporated that its composition is represented by the point F, which lies on the saturation curve of S_1. The solution will, therefore, become saturated first with this salt, and not with the double salt itself as in the previous case. If the evaporation is continued, the salt S_1 will separate and the composition of the complex will be represented by a point between F and J, in the area S_1AC the points of which represent complexes of solid S_1 and a solution on the saturation curve AC. As the composition of the complex approaches that represented by the point J, the composition of the solution will be represented by a point which traverses the saturation curve from F towards C. When so much water has been evaporated that the composition of the complex is given by the point J, formation of the solid double salt will begin, since points between J and D lie in the area S_1CD and represent complexes of both solids S_1 and D in equilibrium with the invariant solution C.

We see, therefore, that an unsaturated solution of the double salt, on concentration, deposits first one of the simple salts, and not the double salt itself. It is usual to say that in such cases the double salt is decomposed by water, although it would be more accurate to say that the double salt is decomposed by solutions represented by points on the saturation curve AC. If, to any solution on this curve, a sufficiently small amount of the double salt is added, the resulting complex will be represented by a point which lies in the area S_1AC, which represents, therefore, solid S_1 in contact with solution. This must mean that S_2 is dissolved out from the double salt, leaving solid S_1 behind. The system formed by water and the double salt alone is not, in this case, a binary system. A mixture of water and the double salt which is represented by a point on the line WD between F and J forms, for example, a phase complex of solid S_1 and a saturated solution of this salt; the composition of the solid phase S_1 cannot, however, be expressed in terms of W and D alone. At the same time, the system W–S_1–S_2 can no longer be considered as built up from the two simpler systems W–S_1–D and W–S_2–D, as an examination of Fig. 21 will show. The system invariant point C no longer lies within the triangle WS_1D or, in other words, the composition of the solution C cannot be expressed in positive terms of water and the two salts S_1 and D with which it is in equilibrium. The following considerations will make this clearer: The proportion of the two simple salts contained by the solution C is equal to that contained by the binary mixture G, and it is therefore:

S_2G parts of S_1 to GS_1 parts of S_2.

The proportion of the same two salts contained by the double salt is:

S_2D parts of S_1 to DS_1 parts of S_2.

The double salt thus contains a greater amount of the salt S_1 in proportion to S_2 than does the liquid C, and it is therefore impossible to express the composition of this solution in terms of water, the double salt, and a positive amount of the salt S_1. The system formed by the solution C in contact with the two salts S_1 and D is in invariant equilibrium at the temperature t and if water is evaporated from it the composition of the solution must remain constant. If the double salt separates from this solution, the latter will become poorer in the salt S_1, since, as we have shown, the double salt contains a greater amount of S_1 in proportion to S_2 than does the solution C. The simultaneous separation of S_1 would only accentuate this alteration in the composition of the solution C, which can clearly only maintain its constant composition by redissolving the simple salt S_1 when the double salt separates.

We will consider the behaviour of the unsaturated solution represented by the point V when water is evaporated from it. The solution will remain unsaturated until it attains the constant composition given by the point K on the saturation curve of S_1, when the solution will become saturated with this salt, and the further evaporation of water will cause it to separate. While the composition of the complex alters from that given by the point K to that given by the point L, solutions will be obtained, in contact with solid S_1, and represented by points on the saturation curve between K and C. When the composition of the complex is represented by the point L, separation of the double salt will begin, and as the point moves from L to M through the area S_1CD, the points of which represent complexes of S_1,D and the solution C, the composition of the solution will remain unaltered, since the conditions are those of invariant equilibrium. We have shown, however, that this cannot occur if further quantities of both the solid salts D and S_1 are deposited; on the contrary, the salt D will alone be deposited and the salt S_1 will be redissolved. Eventually the whole of the solid salt S_1 which was deposited during an earlier stage of the evaporation will be consumed in this way, and we see that when so much water has been evaporated that the composition of the mixture is represented by the point M, this point will enter the area DCE the points of which represent complexes of the *single* solid phase D and a saturated solution. With the loss of a phase, the system will regain a degree of freedom, and as the point representing the composition of the mixture moves from M to N, the composition of the solution will again alter, being represented by a point which traverses the saturation curve of the double salt from C to E. When the composition of the mixture is represented by the point N, the liquid will be saturated both with the double salt and the simple salt S_2, its composition being represented by the point E. On the continued evaporation of water, both these salts will separate and the solution will maintain the constant composition represented by the point E during this last stage of the evaporation, until finally a dry mixture of the double salt D and the simple salt S_2 will be obtained, of the composition represented by the point P. The point E is, therefore, the drying-up point. This invariant point lies within the triangle WS_2D, and the composition of the corresponding solution can therefore be expressed in terms of water and the two salts S_2 and D with which it is in equilibrium. It can then, unlike the solution C, maintain its constant composition by the simultaneous separation of both these salts.

The invariant solution C differs characteristically from the invariant solution E, and from the ternary invariant solutions which we have discussed in the previous paragraphs. It differs in the following respects : Its composition cannot be expressed in terms of water and the two salts with which it is in equilibrium (if only positive concentration values are admitted), and when it is evaporated in contact with these salts, one only is deposited, whilst the other is redissolved. A solution with these properties is said to be incongruently saturated; a ternary invariant solution the composition of which can be expressed in terms of positive amounts of water and the salts with which it is in equilibrium, and which therefore deposits both these salts on evaporation of water, is said to be congruently saturated.

If water is evaporated from the solution represented by the point X in Fig. 21, this solution will become saturated when its composition is represented by the point C. If the evaporation is continued, the point representing the composition of the resulting complex will move through the field DCE the points of which represent the monovariant complexes D + Solution. The Solution C, in the absence of other phases, will therefore deposit only the salt D on the evaporation of water, and the composition of the liquid phase will continue to alter, being represented by a point which traverses the saturation curve of the double salt. We see that the incongruently saturated invariant solution, although it can exist in equilibrium with both S_1 and D, and must, therefore, be considered as saturated with these two salts, yet deposits only one when water is evaporated from it, and it does not maintain its composition unaltered, since, when only two phases are present, the equilibrium is monovariant and not invariant. The solution C can only retain a constant composition on the removal of water, when the solid phase S_1 is also present, because then only will the equilibrium be invariant. The phase reaction which occurs when water is evaporated from the invariant system $D + S_1$ + Solution C results, however, in the dissolution of the solid S_1, and therefore unless a sufficient excess of this solid phase is present, the solution will not maintain the constant composition represented by the point C during the whole process of evaporation to dryness. The straight line joining the point W to any point on the part AF of the saturation curve of S_1, ends on the side S_1S_2 between S_1 and D, *i.e.*, in the area the points of which represent complexes of the two solid salts S_1 and D and the invariant solution C. It follows from this that any solution represented by a point on this part of the saturation curve of S_1 will dry at the constant composition represented by the point C, and therefore that sufficient solid S_1 must have been deposited by the time the composition of the liquid has reached this value to hold the composition constant until complete dryness is reached. It can be seen, in the same way, that solutions represented by points on the part FC of the saturation curve S_1, including the invariant solution itself, will dry at the constant composition represented by the point E. These solutions, therefore, will not deposit sufficient solid S_1 during the first stage of the evaporation to maintain the composition of the liquid phase constant at the value represented by C until complete dryness is reached. The whole of the solid phase S_1 will be consumed by the phase reaction which takes place at the point C before the liquid phase has disappeared; the system will therefore regain a degree of freedom, and the composition of the solution will again alter until it is represented by the point E. The latter invariant solution is congruently saturated, and dries, therefore, at constant composition, separating the two salts S_2 and D.

If the solid which separates from a saturated solution on the evaporation of water is immediately removed from contact with the liquid, then every solution in the system will dry at the constant composition represented by the point E, which is therefore called the final drying-up point. The point C is a drying-up point only in the case where evaporation takes place in presence of excess of solid S_1. The paths of crystallisation on the saturation curves are indicated by the arrows in Fig. 21 and these show clearly that the point C is not a final drying-up point. The arrows on each side of the point C do not converge on it, as was the case in Fig. 20, when this point represented a congruently saturated solution; all arrows converge, in Fig. 21, on the final drying-up point E.

As at the binary system invariant point (§ 18) so too at the ternary isothermal invariant point, the reactions which occur on altering the conditions of equilibrium, are dependent, in cases where a binary compound occurs as a solid phase, upon the relative compositions of the phases in equilibrium. Different phase reactions occur according to whether the composition of the liquid phase can or cannot be expressed in terms of positive quantities of the solids with which it is in equilibrium. Thus we have seen that similar considerations to those which led us to distinguish the eutectic from the transition point in the polythermal binary system, lead us to distinguish the congruently from the incongruently saturated invariant solution in the isothermal ternary system.

§ 31. We shall discuss next the case in which the salts can form crystalline hydrates with water. A considerable number of ternary isothermal types are then possible, but we shall consider in this chapter only the two which are of the most frequent occurrence; a more complete account will be given in Chapter V.

We will suppose that the salt S_1 can form a hydrate, which we denote by H_1, whilst the salt S_2 can form no hydrate. The ternary system W-S_1-S_2 may then show the isothermal type given by Fig. 22. The composition of the hydrate will be represented by a point H_1 on the side WS_1 of the triangle (Fig. 22), such that the length WH_1 gives the percentage of anhydrous S_1, and the length H_1S_1 that of water in the salt hydrate. The point A gives the composition of the saturated solution in the binary system W-S_1 at the temperature t, but this solution is in equilibrium, not with the anhydrous salt S_1, but with the hydrate H_1. Points on the curve AF give the compositions of ternary solutions which are all saturated, not with the anhydrous salt, but with the hydrate H_1. This curve is the saturation curve of the hydrate, and points on it may be joined by conjugation lines to the point H_1, which gives the composition of the solid phase in equilibrium with the solutions which these points represent. Points in the area H_1AF represent the monovariant complexes formed by solid hydrate in equilibrium with a saturated solution.

When the composition of the solution is represented by the point F, the solution itself has become saturated, not only with hydrate H_1, but also with the salt S_2. Complexes of the two solid phases H_1 and S_2 are represented by points on the line H_1S_2, and since these complexes are all in equilibrium with the invariant solution F, points on the line H_1S_2 may be joined by conjugation lines to the point F. Points in the area H_1FS_2 represent, therefore, complexes of the invariant solution F with mixtures of the two solids H_1 and S_2 represented by points on the line H_1S_2.

The invariant point F is also the terminal point of the saturation curve BF, of the salt S_2. As before, the point B gives the composition of the saturated solution in equilibrium with solid S_2 in the binary system W–S_2 at the temperature t, and points in the area S_2BF represent the monovariant complexes S_2 + Solution.

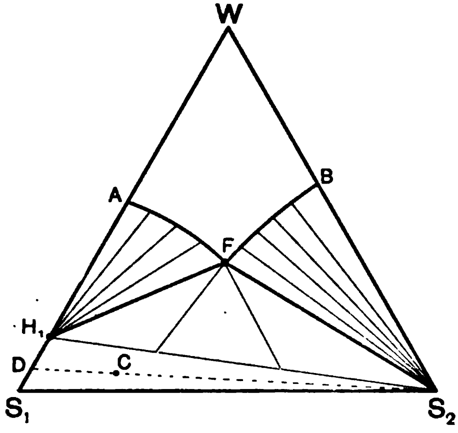


FIG. 22.

The proportion of water to S_1 contained in the mixture represented by the point C is S_1D parts of water to DW parts of S_1. The mixture contains, therefore, less water in proportion to anhydrous S_1 than does the solid hydrate, in which the proportion is S_1H_1 parts of water to H_1W parts of S_1. There is, in other words, not sufficient water present in the mixture represented by the point C to produce complete hydration of the salt S_1, and no stable solution can exist in these circumstances. This is true of every mixture represented by a point in the area, $H_1S_1S_2$, and these points represent, therefore, the completely solid complexes $H_1 + S_1 + S_2$.

§ 32. The isotherm depicted in Fig. 22 is of the simplest type which can occur in the case where one of the salts forms a hydrate. A second possible isothermal type is illustrated in Fig. 23. The point A represents, as before, the composition of the solution saturated with the hydrate H_1 at the temperature t, in the binary system W–S_1. AE is the saturation curve of the hydrate, and AH_1E the complex area of solid hydrate and saturated solutions. Now on the continued addition of S_2 to saturated solution in contact with H_1, a point may be reached at which the added salt S_2 dissolves only by extracting water from the solid hydrate, which is thereby dehydrated to the anhydrous salt S_1. As soon as this point is reached, two solid phases—the hydrate H_1 and the anhydrous salt S_1—are present in contact with a solution; this solution must therefore be invariant in composition, and it is represented in Fig. 23 by the point E.

On the addition of solid S_2 to the solution E in contact with the solid hydrate H_1, the added salt will react with the hydrate, forming a liquid of the same composition as that represented by the point E, and precipitating anhydrous S_1; this reaction will leave the composition of the liquid phase unaltered. Mixtures of the hydrate with anhydrous S_1 are represented by points on the line H_1S_1, between H_1 and S_1. Conjugation lines which terminate at one end in the invariant point E must therefore terminate at the other end in a point on the line H_1S_1; points in the area H_1ES_1 represent, accordingly, complexes of the solution E in contact with the two solids H_1 and S_1.

As long as undecomposed hydrate is still present, the solution will retain the composition represented by E, but as soon as sufficient S_2 has been added to dehydrate completely the existing solid hydrate, the system will regain a degree of freedom owing to the disappearance of this as a solid phase. On the continued addition of S_2, the composition of the solution will therefore again alter, and the point which represents it will traverse the curve EF the points of which give the composition of solutions saturated only with the solid S_1. This curve is the saturation curve of the anhydrous salt S_1, and S_1EF is the area of complexes formed from solid anhydrous S_1 and saturated solutions represented by points on the curve EF. The saturation curve of S_1 ends in the point F, where the solution becomes saturated also with S_2. The point F represents the invariant solution which is in equilibrium with both solids S_1 and S_2, and points in the area S_1FS_2 represent complexes of these two solid salts and the solution F. The curve BF is, as before, the saturation curve of S_2 and S_2BF the complex area of solid S_2 and saturated solutions represented by points on the curve BF.

and saturated solutions. Now on the continued addition of S_2 to saturated solution in contact with H_1, a point may be reached at which the added salt S_2 dissolves only by extracting water from the solid hydrate, which is thereby dehydrated to the anhydrous salt S_1. As soon as this point is reached, two solid phases—the hydrate H_1 and the anhydrous salt S_1—are present in contact with a solution; this solution must therefore be invariant in composition, and it is represented in Fig. 23 by the point E.

On the addition of solid S_2 to the solution E in contact with the solid hydrate H_1, the added salt will react with the hydrate, forming a liquid of the same composition as that represented by the point E, and precipitating anhydrous S_1; this reaction will leave the composition of the liquid phase unaltered. Mixtures of the hydrate with anhydrous S_1 are represented by points on the line H_1S_1, between H_1 and S_1. Conjugation lines which terminate at one end in the invariant point E must therefore terminate at the other end in a point on the line H_1S_1; points in the area H_1ES_1 represent, accordingly, complexes of the solution E in contact with the two solids H_1 and S_1.

As long as undecomposed hydrate is still present, the solution will retain the composition represented by E, but as soon as sufficient S_2 has been added to dehydrate completely the existing solid hydrate, the system will regain a degree of freedom owing to the disappearance of this as a solid phase. On the continued addition of S_2, the composition of the solution will therefore again alter, and the point which represents it will traverse the curve EF the points of which give the composition of solutions saturated only with the solid S_1. This curve is the saturation curve of the anhydrous salt S_1, and S_1EF is the area of complexes formed from solid anhydrous S_1 and saturated solutions represented by points on the curve EF. The saturation curve of S_1 ends in the point F, where the solution becomes saturated also with S_2. The point F represents the invariant solution which is in equilibrium with both solids S_1 and S_2, and points in the area S_1FS_2 represent complexes of these two solid salts and the solution F. The curve BF is, as before, the saturation curve of S_2 and S_2BF the complex area of solid S_2 and saturated solutions represented by points on the curve BF.

The second salt S_2 may also form a hydrate H_2 at the temperature considered, and this hydrate may or may not be dehydrated by the addition of the hydrate H_1 to solutions in equilibrium with H_2. The isothermal types, in these cases, can be deduced by the reader with the help of the examples already given.

As another possibility, the hydrate H_1 may be dehydrated by the addition of the second salt to its saturated solution, yielding, not the anhydrous salt S_1, but a lower hydrate h_1, which contains a smaller percentage of water than does the hydrate H_1. At a still higher concentration of the second salt in the liquid phase, the hydrate h_1 may be completely dehydrated to the anhydrous salt S_1. The isotherm will, in this case, show two saturation curves, that of h_1, and that of S_1, inserted between the saturation curves of H_1 and S_2, which are the stable solid phases in equilibrium with the two binary saturated solutions at the temperature t.

§ 33. A compound may occur in the ternary system the composition of which can be expressed only in terms of all three components; such a compound is said to be a ternary compound. A double salt, which forms a hydrate containing water of crystallisation, is, for example, a ternary compound, and it must clearly be represented by a point such as D (Fig. 24) which lies within the triangle.

Here again a large number of isothermal types may occur, and these will be discussed more fully in Chapter V. The isotherm of Fig. 24 depicts the case in which the simple salt S_1 forms a hydrate H_1, the salt S_2 being anhydrous at the temperature of the isotherm, whilst the two salts form a hydrated double salt D of the general formula $mS_1 . nS_2 . pW$, where m, n, and p are whole numbers giving the molecular proportion in which the three components combine, and defining, therefore, the position of the point D in the triangle.

Since the hydrated double salt occurs as solid phase at the temperature t, it must possess its own saturation curve in the isotherm. This is the curve CE which lies between the two saturation curves AC and BE, of H_1 and S_2 respectively. Points on it represent the compositions of solutions saturated with the hydrated double salt, and conjugation lines may therefore be drawn joining these points to the point D. The saturation curve of the hydrated double salt ends, on the one side, in the invariant point C, which represents the composition of the solution in equilibrium with the two solid phases $D + H_1$, and on the other side, in the invariant point E which represents the composition of the solution in equilibrium with the two solid phases $D + S_2$.

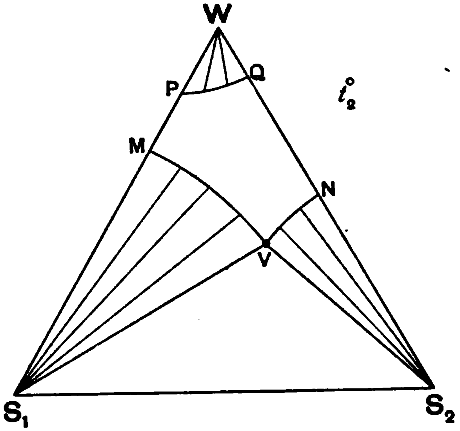
The line DW in Fig. 24 intersects the saturation curve of the hydrated double salt, and hence this salt is not decomposed by water, and both the isothermal invariant points C and E represent congruently saturated solutions. The case may, however, occur in which the hydrated double salt is decomposed by water, one of the invariant solutions being incongruently saturated.

We see that when a compound occurs as a solid phase in the ternary system, a number of possible isothermal types arise. If, for example, a salt hydrate is formed, this may or may not suffer dehydration in the ternary system at constant temperature, or if a hydrated or anhydrous double salt is formed, it may or may not be decomposed by water. We shall see later that, as the temperature changes, so the isotherm may pass from one type to another through certain transition forms. We must, however, first consider the effects of temperature changes upon the isothermal type in the simplest case, namely, that in which no compounds, but only the components themselves, can occur as solid phases.

§ 34. The three binary systems the components of which are respectively $W\text{–}S_1$, $W\text{–}S_2$, and $S_1\text{–}S_2$ may be considered to form the basis of the ternary system $W\text{–}S_1\text{–}S_2$.

The conditions of equilibrium in the binary system $W\text{–}S_1$, at all temperatures at which a liquid phase can exist, are represented in Fig. 25, for the simple case in which no binary compound occurs. The point A represents water at its freezing point, in equilibrium with ice, and it corresponds, therefore, with a temperature of 0°. The curve AB is the polythermal saturation curve of ice in this binary system, and points on it give the compositions of binary solutions which are in equilibrium with ice at various temperatures.

The point C represents the solid salt S_1 in equilibrium, at its melting point t_{12}, with the pure liquid salt. The curve CB is the polythermal saturation curve of S_1 in this binary system, and points on it give the compositions of binary liquids in equilibrium at various temperatures, with solid S_1. The point B represents the eutectic solution which is in equilibrium with



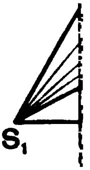
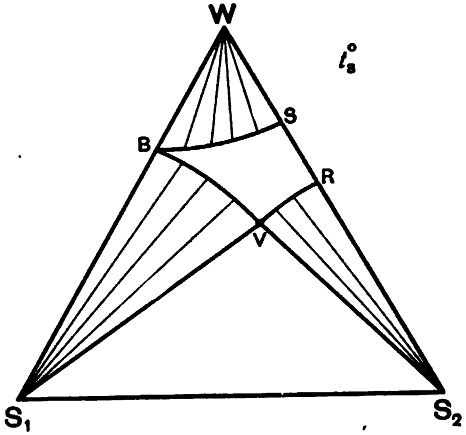


Fig. 29.



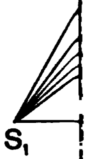


Fig. 31.

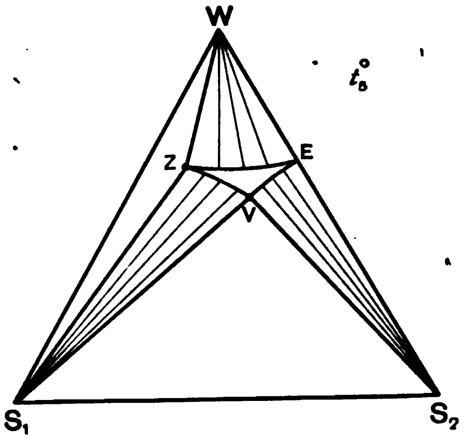


Fig. 33.

SHEET IV.

both ice and solid S_1 at the eutectic temperature t_3, in the binary system W–S_1.

The binary system W–S_2 is similarly represented in Fig. 26. The points A and F give, respectively, the melting points of ice and of the salt S_2, and we shall assume that the melting point t_1, of this salt is lower than the melting point t_{12} of the salt S_1. The curves DE and FE are the polythermal saturation curves of ice and S_2 respectively, in this binary system. The point E represents the binary eutectic solution which is in equilibrium with ice and solid S_2 at the corresponding eutectic temperature t_5, and we shall assume that this temperature is lower than the eutectic temperature t_3 in the system W-S_1.

We will now consider the isotherm in the ternary system W-S_1-S_2 at a variety of temperatures, and we shall begin with the temperature t_1, which is lower than the melting points of the pure salts, and higher than that of ice.

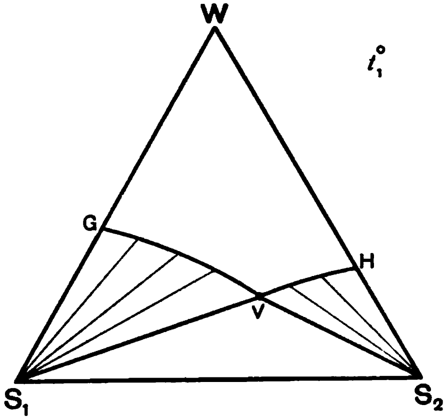


FIG. 28.

The ternary isotherm at this temperature is represented in Fig. 28; it belongs to the simple type which we have already discussed. A line of constant temperature t_1, in the binary system W-S_1 (Fig. 25), cuts one saturation curve only, namely, BC, that of S_1, and the point of intersection G gives the composition of the liquid which is saturated with S_1 at this temperature in the binary system. It is the only saturated solution which exists at this temperature in the binary system W-S_1, and its composition is represented in the ternary isotherm (Fig. 28) by the point G on the side WS_1 of the triangle. The point H in the binary system W–S_2 (Fig. 26), and on the line WS_2 of the ternary isotherm (Fig. 28), represents similarly the composition of the binary solution saturated with S_2 at the temperature t_1. We have already seen that the isothermal saturation curves GV and HV, which represent the compositions of ternary solutions saturated with S_1 and S_2 respectively, diverge from these two points, and intersect in a point V, which represents a ternary solution saturated with both salts at the temperature t_1.

Now, if we lower the temperature below t_1, no change will at first occur in the type of the isotherm. The only effect will be that the points G and H will move closer to the water corner, corresponding with the decreasing concentration of the salts in their binary saturated solutions due to the falling temperature.

Suppose, now, that the temperature is lowered to a point t_2, below the melting point of ice, but still above both binary eutectic temperatures. The constant temperature line t_2 in the binary system W–S_1 (Fig. 25) is now seen to cut both binary saturation curves. There are accordingly two saturated solutions in the binary system at this temperature, the one P saturated with ice, and the other M with the salt S_1. The compositions of both these saturated solutions are represented also by the points P and M on the side WS_1 of the triangle in Fig. 29, which gives the ternary isotherm at the temperature t_2. For a similar reason—namely, that the constant temperature line cuts both the ice and the salt binary saturation curves—there are two saturated solutions, Q and N, in the binary system W–S_2 at the temperature t_2, and these are represented on the side WS_2 of the triangle. Of these, the solution Q is saturated with ice, and the solution N with the salt S_2.

Now, as before, the point M is a terminal point of the isothermal saturation curve which represents a series of ternary solutions all saturated, or in equilibrium, with solid S_1, and N is a terminal point of the ternary saturation curve of solid S_2 at the temperature t_2. In exactly the same way, the points P and Q, which represent binary solutions in equilibrium with the same solid phase, are *both* terminal points of a third ternary saturation curve, that of ice. They lie at the extremities of a continuous saturation curve PQ, every point of which represents the composition of a ternary solution in equilibrium with ice, and may therefore be joined by a conjugation line to the water (or ice) corner. This isotherm clearly differs in type from that which we have first considered. It is characterised by the fact that it exhibits a third saturation curve—that of ice; another complex area WPQ is thereby introduced, the points of which

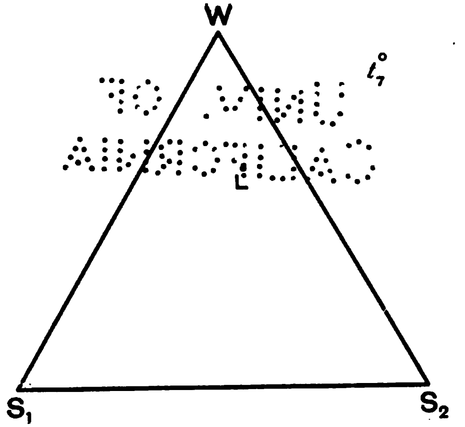


FIG. 35.

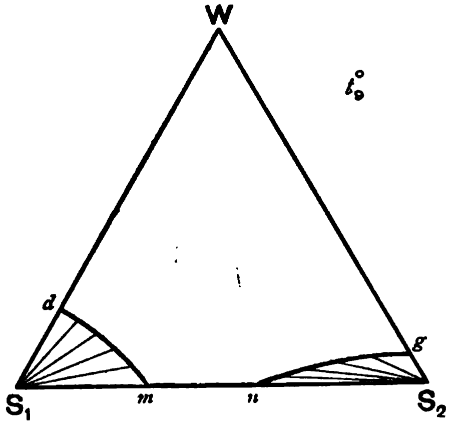


FIG. 37.

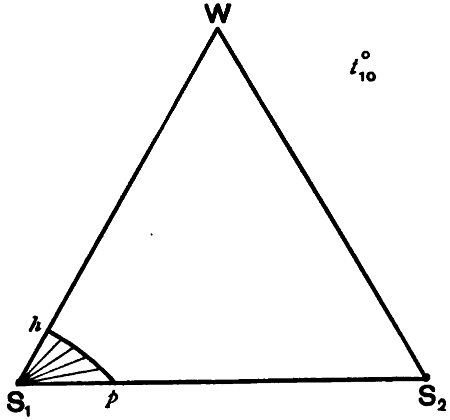


FIG. 39.

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represent phase complexes of solid ice and solutions in equilibrium with it. This new complex area restricts the area of unsaturated solutions, which is now represented by *PQNVM*.

It will be seen from the binary polytherms (Figs. 25 and 26) that the change in the isothermal type must occur at 0°, for this is the highest temperature in each binary system, at which a constant temperature line cuts both binary saturation curves. At this temperature (0°), the ice saturation curve is cut in a point *A* representing pure water. Pure water is here in equilibrium with ice and, treating this as a limiting case, we may say that the point *A* represents a liquid phase saturated with ice in the unary system formed by water. The water corner itself represents, therefore, the composition of a saturated solution in the ternary isotherm at 0° (Fig. 30), and it is the only point in the whole isotherm which represents a liquid phase saturated with ice. The saturation curve of ice may be considered as growing out from it as the temperature is lowered below 0°, or as shrinking up into it as the temperature is raised from lower ranges, to 0°.

If we lower the temperature below t_2, the points *P* and *M* (Fig. 25) and *Q* and *N* (Fig. 26) clearly approach one another. At the binary eutectic temperature t_3, in the system W-S_1, the points *P* and *M* coincide in the point *B*, which represents a solution saturated with both ice and the salt S_1.

The ternary isotherm for the temperature t_3 is depicted in Fig. 31. The binary solution represented by the point *B* on the side WS_1 represents now a solution saturated with both ice and S_1, and hence it must be the terminal point of two ternary saturation curves. The saturation curve of ice and that of S_1 meet on the side WS_1 of the triangle, in the point *B*. As the temperature is supposed to be still above the eutectic temperature t_5 in the system W–S_2, there will still be two saturated solutions in this binary system ; these are represented by the points *S* and *R* in Fig. 26, and the ternary saturation curves of ice and S_2 in Fig. 31 terminate on the side WS_2, in these points.

At a temperature t_4, still lower than t_3, and still above the eutectic temperature t_5, the isothermal relations are those shown in Fig. 32. At this temperature, as may be seen from Fig. 25, no solution can exist in the binary system W–S_1, and therefore no saturation curve, in Fig. 32, can cut the side WS_1 of the triangle. The ternary saturation curves of ice and of S_1 must therefore intersect in a point Z *within* the triangle, and since this point lies on both saturation curves, it must represent a ternary solution in equilibrium with both ice and solid S_1. The system formed by the solution Z in equilibrium with the two solid phases ice and S_1 is in a state of invariant equilibrium at constant temperature, and the point Z is, therefore, a second isothermal invariant point. Points in the area WZS_1 represent complexes of ice, solid S_1 and the invariant solution Z, whilst the field of unsaturated solutions is still further restricted to the area $UZVX$. This type of isotherm is characterised by the possession of two invariant points, and it represents the conditions which obtain at any temperature between the two eutectics t_3 and t_5. The isotherm of Fig. 31 is merely a transition type between those of Figs. 29 and 32; it obtains only at the definite eutectic temperature t_3, in the binary system W–S_1. As we have already pointed out, the change from the isothermal type of Fig. 28 to that of Fig. 29 is similarly marked by a transition type; it is the 0° isotherm (Fig. 30), in which the water corner itself represents a saturated solution. This particular transition type holds only for the definite temperature, the melting point of ice. Every change in the isothermal type is preceded in this way by a special transition type which holds only at a definite temperature—either at the melting temperature of one of the components, or at the eutectic temperature in one of the binary systems.

The type shown in Fig. 32 will clearly persist until the temperature is lowered to t_5, the eutectic temperature in the second binary system W–S_2, when the isotherm will show the transition form depicted in Fig. 33. The saturation curves of ice and solid S_2 will meet on the side WS_2, at the eutectic point E in the system W–S_2. At a temperature below t_5, it can be seen from Figs. 25 and 26 that no solutions can exist either in the system W–S_1, or in the system W–S_2. The isotherm at the temperature t_6 (which is below t_5) is depicted in Fig. 34. All the saturation curves lie entirely within the triangle. The saturation curve of ice and of solid S_2 intersect inside the triangle at the point Y, which represents a solution saturated with both ice and S_2. The system formed by the solution Y in equilibrium with the two solid phases ice and S_2 is in a state of invariant equilibrium at the temperature t_6, and this isothermal type is therefore characterised by the possession of a third invariant point Y, and a new complex area YWS_2, the points of which represent complexes of the solution Y and the two solids ice and S_2. The field of unsaturated solutions is still further reduced to the enclosed area ZVY.

As the temperature is further lowered, the area of unsaturated solutions will become smaller and the three invariant points Z, Y, and V will continuously approach one another, until finally, at a certain temperature t_7, they will coincide in one point L; the isotherm at this temperature is given in Fig. 35. At the temperature t_7 the three invariant points, and the three saturation curves have all shrunk into the point L, and this point represents, therefore, the composition of a solution which is saturated at the temperature t_7 with all three solid phases $S_1 + S_2 +$ Ice.

We have shown in § 21 that when three solid phases are in equilibrium with a ternary solution the system is in a state of invariant equilibrium. It will now be necessary to distinguish carefully between the isothermal invariant point and the system invariant point. The points Z, Y, and V of Fig. 34 are isothermal invariant points, *i.e.*, they represent, at the temperature t_6, the compositions of solutions in the systems Ice $+ S_1 +$ Solution, Ice $+ S_2 +$ Solution, and $S_1 + S_2 +$ Solution; these systems are in invariant equilibrium only if the temperature is constant. When the temperature is lowered below t_6, the compositions of the solutions in these three isothermally invariant systems, alter, and the three points which represent these compositions approach one another. At the temperature t_7 they coincide in the point L, which represents the solution in equilibrium with all three solid phases. Now the system $S_1 + S_2 +$ Ice $+$ Solution L is in a state of invariant equilibrium at constant pressure (not constant pressure and temperature), and none of the conditions of equilibrium can be chosen arbitrarily. The system can only remain in equilibrium at the temperature t_7, and the point L is the system invariant point giving the composition of the single invariant solution which is in equilibrium with the three solid components in the system W–S_1–S_2.

If heat is abstracted from the invariant system in equilibrium at the temperature t_7, neither the temperature nor the composition of the liquid phase will alter. The liquid will deposit all three solid components in the same proportion as that in which it contains them, *i.e.*, the following phase reaction will occur :

$$\text{Solution } L \rightarrow S_1 + S_2 + \text{Ice},$$

and this reaction can clearly maintain the constant composition of the liquid phase. The temperature will not begin to fall on the withdrawal of heat until this phase has been completely consumed by the reaction, and there will remain a solid complex of the three phases $S_1 + S_2 + \text{Ice}$. The temperature t_7, of the system invariant point L, is, therefore, a lower temperature limit to the existence of a liquid phase in the ternary system it is, in other words, the ternary eutectic point.

The isothermal type shown in Fig. 34 will persist until the ternary eutectic temperature t_7 is reached, when the isotherm will show the transition form of Fig. 35. The point L in this figure represents the composition of the ternary eutectic solution, and every other point within the triangle represents a phase complex of one, two, or all of the three solids ice, S_1 and S_2 with the solution L.

Below the temperature t_7, there will be neither saturation curves nor points in the isotherm, since no solution can exist. Every point in the triangle will therefore represent a solid complex of S_1, S_2, and Ice.

We have now studied the typical isothermal changes involved when, starting from the temperature t_1 and the simple isothermal type of Fig. 28, the temperature is lowered to that of the ternary eutectic point t_7. Four isothermal types can be distinguished, which are differentiated by the following characteristics :

1. The isotherm contains two saturation curves and one invariant point (Fig. 28).
2. The isotherm contains three saturation curves and one invariant point (Fig. 29).
3. The isotherm contains three saturation curves and two invariant poin's (Fig. 32).
4. The isotherm contains three saturation curves and three invariant points (Fig. 34).

Separating these, and existing at the various unary and binary invariant temperatures, are the four transition forms shown in Figs. 30, 31, 33, and 35.

§ 35. We will next consider the behaviour of the system when the temperature is raised above t_1. No further change will occur in the isothermal type until another binary eutectic temperature is reached, that is, until the temperature reaches that of the eutectic point in the binary system S_1–S_2. We have not so far considered this system, the reason being that we have dealt with temperatures below those at which the salt mixtures fuse—temperatures at which all mixtures of the two salts were solid. No liquid phase could therefore exist in the binary system S_1–S_2, and no saturation curves could cut the corresponding side of the triangle in the ternary isotherm.

The binary system S_1–S_2 in its simplest form is represented in Fig. 27. The point C is, as before, the melting point of pure S_1, the point F that of pure S_2, and the point T represents the eutectic solution, or melt, with which both solids S_1 and S_2 can exist in equilibrium at the eutectic temperature t_8. The curves CT and FT are the saturation curves of S_1 and S_2 respectively, in the binary system S_1–S_2.

Now, if we consider the isotherm in the ternary system W–S_1–S_2 at the temperature t_8 (Fig. 36), we shall see that the ternary invariant point which represents the solution in equilibrium with the two solids S_1 and S_2 must actually fall on the side S_1S_2 of the triangle. At the eutectic temperature t_8, the two solid phases S_1 and S_2 can exist in equilibrium with a liquid in the *binary* system, and hence the saturation curves of S_1 and S_2 in the ternary isotherm must meet on the side S_1S_2, at the point T, which gives the composition of the binary eutectic liquid.

Fig. 36 represents an isothermal transition form. The type of Fig. 28 will persist until this temperature is reached; the invariant point which represents the solution in equilibrium with both solids S_1 and S_2 will approach closer to the side S_1S_2 as the temperature rises, until at this temperature it lies on that side. At temperatures above t_8, the isothermal type will change to that of Fig. 37. It can be seen from Fig. 27 that at the temperature t_9, above t_8, two saturated liquids can exist in the binary system S_1–S_2, namely, that represented by the point m, which is in equilibrium with solid S_1, and that represented by the point n, which is in equilibrium with solid S_2. These two saturated solutions are represented by the points m and n on the side S_1S_2 of the triangle in the ternary isotherm at t_9 (Fig. 37). There still exist, at this temperature, one solution in the binary system W–S_1, which is saturated with S_1, and is represented by the point d, and one solution in the binary system W–S_2, which is saturated with S_2, and which is represented by the point g.

The points d and m must both lie on the ternary saturation curve of S_1, since they both represent solutions in equilibrium with this salt, and similarly the points g and n must both lie on the saturation curve of S_2. The two saturation curves extend, therefore, continuously from one side of the triangle to another, from d, the point which represents the saturated solution of S_1 in the system W–S_1, to m, the point which represents the melt saturated with S_1 in the anhydrous system S_1–S_2; and from g, the point which represents the saturated solution of S_2 in the system W–S_2, to n, the point which represents the liquid phase in equilibrium with the same salt in the system S_1–S_2. Since these curves do not intersect within the triangle, there is no ternary invariant solution at this temperature; the two solids S_1 and S_2 cannot exist together in equilibrium with a liquid phase. There are only three areas in this isotherm, namely, the large area of unsaturated solutions $Wdmng$, the area S_1dm, the points of which represent complexes of solid S_1 and saturated solutions represented by points on the curve dm, and the area S_2gn, the points of which represent complexes of solid S_2 and saturated solutions represented by points on the curve gn.

On raising the temperature still further, the type of Fig. 37 will persist until the melting temperature t_{10} of pure S_2 is passed. The isotherm for a temperature such as t_{11}, above t_{10}, is given in Fig. 38. At this temperature, there is only one saturated liquid in the system S_1–S_2; it is the liquid represented by the point q, and in equilibrium with solid S_1. There still exists one saturated liquid in the binary system W–S_1, namely, the liquid represented by the point l, also in equilibrium with solid S_1. No saturated solution exists in the binary system W–S_2 at this temperature, since the salt S_2 cannot exist as a solid phase at a temperature above its melting point;

hence there is no saturation curve of S_2 in the ternary isotherm, which consists only of the saturation curve lq of S_1, the large area $WlqS_2$ of unsaturated solutions, and the area S_1lq, the points of which represent complexes of the solid S_1 and saturated solutions represented by points on the curve lq. The transition form from the preceding type to the present type is given in Fig. 39, and holds only for the particular temperature t_{10}, the melting point of the salt S_2. In this isotherm the corner S_2 itself represents a saturated liquid, for at this temperature pure liquid S_2 is in equilibrium with solid S_2; it is the only point in the isotherm which represents a liquid in equilibrium with this solid phase. The saturation curve of S_2 grows out from this point with decreasing temperature, or vanishes into it with increasing temperature, exactly as was the case with the ice saturation curve and the water corner at a lower temperature.

As the temperature rises above t_{11}, so the points l and q (Fig. 38) will approach the S_1 corner, until the melting point t_{12} of pure S_1 is reached. At this temperature the isotherm will possess the transition form shown in Fig. 40. Pure liquid S_1 is here in equilibrium with solid S_1, and the saturation curve of S_1 has therefore dwindled into the S_1 corner. The point S_1 represents, moreover, the only liquid which can be in equilibrium with a solid at this temperature; it is, in other words, the only point in the isotherm which represents a saturated solution, and every other point represents an unsaturated solution. At temperatures above t_{12}, no solid can exist in the system W–S_1–S_2, and every point in the triangle represents an unsaturated liquid.

We have now described two more isothermal types, with the following characteristics:

5. The isotherm contains two saturation curves and no invariant point (Fig. 37).

6. The isotherm contains one saturation curve and no invariant point (Fig. 38).

In addition there are the three transition types shown in Figs. 36, 39, and 40.

We saw in the previous chapter that the polythermal saturation curves in the simple binary systems extend continuously to the melting points of pure salts only if the salts are not decomposed by water, if two liquid layers are not formed, and if the critical temperatures of binary mixtures are not attained.

The series of ternary isotherms which we have deduced theoretically will also be realised in practice only when these same conditions hold.

The series refers strictly to one constant pressure in the condensed system, but since we are considering only the conditions of equilibrium between solid and liquid phases, this limitation need not be observed in practice, provided that too great variations in the pressure do not occur. Thus the series of isotherms may be partly constructed from the results of experimental investigations carried out at atmospheric pressure, and in the presence of a vapour phase.

At high temperatures the liquid phase, strictly unstable in the presence of vapour at pressures different from its own vapour pressure, will evaporate too quickly to admit of this method of experimental investigation.

The two isothermal types shown in Figs. 37 and 38 cannot, in general, be realised experimentally by working in open vessels under atmospheric pressure. The vapour pressure of solutions at the high temperatures where these types obtain will nearly always be far above one atmosphere, and the temperatures will therefore be above the boiling points of the solutions under atmospheric pressure. The experimental investigation of these types must take place, therefore, in sealed vessels, and very often under considerable pressure.

§ 36. We must next consider how these various isothermal types can be incorporated into one figure, which shall give the conditions of equilibrium in the system W–S_1–S_2, at all temperatures at which a liquid phase can exist.

In order to accomplish this, we must have recourse to a representation in space. It is not possible to represent, in a plane figure, the variations of more than two independent factors. We have succeeded in representing inside the triangle the simultaneous variations of all three concentration factors, but this arises from the fact that only two of these are really independent variables. The third concentration factor is fixed by the other two, and is therefore dependent on them, being the difference between 100 and their sum. Temperature is a third independent variable, and the relation between

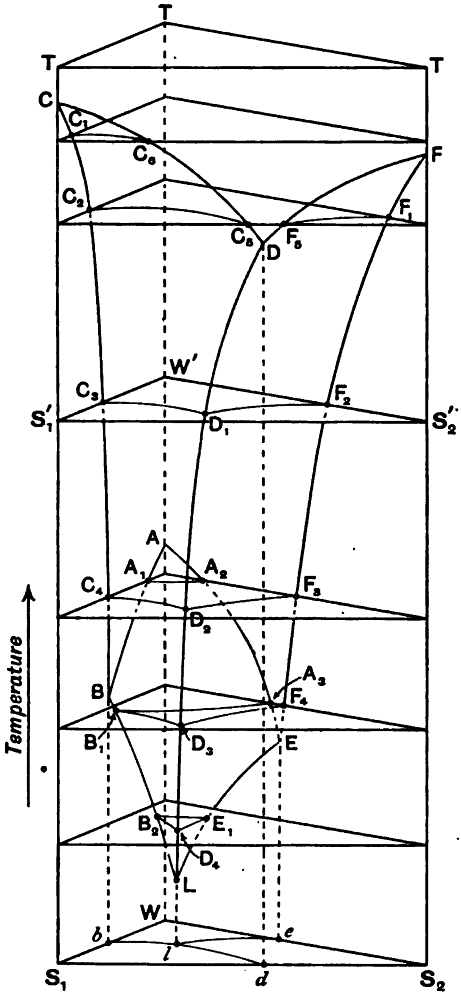
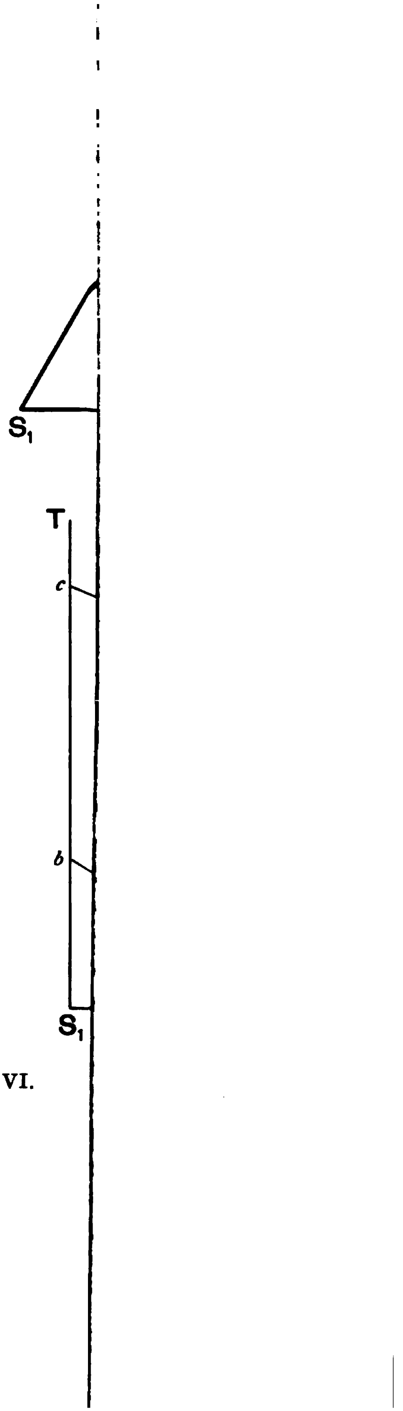


FIG. 41.



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it and the composition of saturated solutions can only be expressed completely by means of a three dimensional figure.

We shall represent the system by a figure lying inside a right triangular prism TWS_1S_2 (Fig. 41). The base of this prism is formed by the equilateral triangle WS_1S_2, which is to be considered as lying in a horizontal plane. Temperature will be measured vertically upwards, along the parallel edges of the prism, which are perpendicular to the plane of the base.

Points on the edge WT are taken to represent pure water at various temperatures; similarly points on the edges S_1T and S_2T represent the pure salts S_1 and S_2 at various temperatures.

We saw that, in the ternary isotherm, the conditions of equilibrium in the binary system W–S_1 *at the fixed temperature of the isotherm*, were represented on the side WS_1 of the triangle. In the same way, the conditions of equilibrium in this binary system *at all possible temperatures* will be represented on the side face TWS_1 of the prism, in the ternary polytherm (Fig. 41). The polythermal saturation curves in the binary system W–S_1, which are represented in the plane of the paper in Fig. 25, are reproduced on the face TWS_1 of the prism in Fig. 41. The point C gives the melting point of the pure salt S_1, A that of ice; the curve CB is the binary saturation curve of S_1, and AB that of ice, whilst the point B represents the eutectic solution in equilibrium with both ice and solid S_1 in the binary system W–S_1. In the same way, the binary system W–S_2 is represented on the side face TWS_2, which corresponds therefore with Fig. 26. The point F gives the melting point of the salt S_2, the point E represents the eutectic solution in equilibrium with both ice and solid S_2, whilst AE and FE are the binary saturation curves of ice and S_2 respectively, in the system W–S_2. Finally, the binary system S_1–S_2 of Fig. 27 is represented on the front face TS_1S_2 of the prism. The point D represents the eutectic melt in this system, which is in equilibrium with both solids S_1 and S_2, whilst CD and FD are the binary saturation curves of S_1 and S_2 respectively. It is clear that, in nearly all cases, the temperatures corresponding with the points C, F, and D will be very much higher than those corresponding with the points A, B, and E, as represented in Fig. 41.

All points inside the prism represent ternary mixtures of W, S_1, and S_2 at various temperatures. Let us consider, as an example, the point D_1, which is supposed to lie in the interior of the prism. A plane $W'S'_1S'_2$ is laid through the point D_1, parallel to the base WS_1S_2 of the prism. Now the point D_1 represents a ternary mixture the composition of which is defined by the position of the point in the triangle $W'S'_1S'_2$ in the usual way, and the temperature of which is given by the height WW' of the plane containing D_1 above the base of the prism. A horizontal triangular section of the prism, such as $W'S'_1S'_2$, is a constant temperature section, since every point on it is at the same height above the base; in other words, the typical isotherms which we have already discussed represent sections of the space figure at various heights. We could then clearly build up the space figure by superimposing the typical isotherms, in the order of increasing temperatures. We shall not, however, adopt this course, but we shall first deduce the form of the space figure from general considerations, and shall show subsequently that sections at various heights do actually give the typical isotherms.

We have seen already that the lowest temperature at which a liquid phase can exist is that of the invariant system formed by the three solid components ice, S_1 and S_2 in equilibrium with a ternary liquid phase, which we have called the solution L in § 34. This solution is represented in Fig. 41 by the point L, which lies within the prism, and is the ternary eutectic point; it is, therefore, the lowest point in our space figure.

If heat is added to the invariant system

$$\text{Ice} + S_1 + S_2 + \text{Solution } L,$$

the temperature will not alter, but the three solids will melt in such a way as to leave the composition of the solution unchanged; the following phase reaction will occur:

$$\text{Ice} + S_1 + S_2 \rightarrow \text{Solution } L.$$

When one of the solid phases has been consumed by this reaction, the system will gain a degree of freedom, the temperature can then rise, and the composition of the liquid can alter.

At temperatures above that of the eutectic point, the three following monovariant systems can therefore exist:

Ice + S_1 + Solution . . . . . . 1.
Ice + S_2 + Solution . . . . . . 2.
and S_1 + S_2 + Solution . . . . . . 3.

These are the three systems which we have considered in the foregoing paragraphs at constant temperature, when they were in a state of invariant equilibrium. Since we no longer impose this restriction on the temperature, we must now consider them as monovariant.

In the system 1 formed by the two solids Ice and S_1 in equilibrium with a ternary solution, there will correspond a definite composition of this solution with every temperature in the range of existence of the system. The compositions of solutions in equilibrium with these two solids will therefore be represented by the points on a curve such as *LB* in Fig. 41, which rises from the eutectic point *L* and is cut in one point (the isothermal invariant point) by every isothermal section in the temperature range. This curve may be considered as the locus of the isothermal invariant point with varying temperatures, and we see that the polythermal saturation curve in the ternary system represents the compositions of solutions in equilibrium, not with one, but with two solid phases. We showed in the discussion of isothermal types (§ 34) that the highest temperature at which an isothermal invariant point can occur, representing a solution in equilibrium with the two solid phases Ice + S_1, is that of the binary eutectic point in the system W–S_1, when these two solid phases are in equilibrium with a binary invariant solution. The polythermal saturation curve of Ice + S_1 in the ternary system rises, therefore, from the ternary eutectic point *L*, and reaches its temperature maximum in the point *B* (Fig. 41), which is the eutectic point in the binary system W–S_1. We may consider the ternary eutectic point *L* as giving the common melting point of the three solids Ice + S_1 + S_2, the binary eutectic point *B* as giving the common melting point of the two solids Ice + S_1, and the polythermal saturation curve *BL* as giving the lowering of the common melting point of Ice + S_1, due to the addition of increasing amounts of the third component S_2. This view is analogous to that which considers the binary saturation curve CB as giving the lowering of the melting point of the pure salt S_1 due to the addition of increasing amounts of the second component, water.

The compositions of solutions in the monovariant system 2 are represented by points of the polythermal saturation curve LE of the two solids Ice + S_2. This curve rises from the ternary eutectic point L, which represents a solution in equilibrium, not only with these two solids, but also with S_1, and it ends in the binary eutectic point E, which represents a solution in equilibrium with the two solids in the binary system W–S_2. It can be considered as giving the lowering of the common melting point of Ice + S_2 due to the addition of increasing amounts of the third component S_1.

Finally, points on the curve LD represent the compositions of solutions in the monovariant system 3. This curve is the polythermal saturation curve of $S_1 + S_2$, and it also rises from the point L, reaching its temperature maximum in the corresponding binary eutectic point D, which lies on the front face of the prism and represents the fused salt mixture in equilibrium with the two solid salts in the binary system S_1–S_2. It is clear that this saturation curve has much the greatest temperature range.

In the ternary isotherm within a certain temperature range there exists a curve every point of which represents a solution saturated with one particular solid. These solutions must be represented in the space figure by points which lie on a surface the intersection of which with every isothermal plane inside that range is a definite curve—the isothermal saturation curve of that particular solid at that particular temperature. Solutions saturated with one solid must therefore be represented in the space figure by points on a saturation surface, and we may consider such a surface as being traced out by the isothermal saturation curve when the temperature is continuously altered.

In Fig. 41, the saturation surface of solid S_1 is given by $CDLB$, a surface which is bounded by the four saturation curves also representing solutions saturated with solid S_1. These curves are: (1) the binary saturation curve CD on the front face of the prism, representing the fused salt mixtures which are in equilibrium with solid S_1 in the system S_1–S_2; (2) the binary saturation curve *CB* on the side face of the prism, representing aqueous solutions in equilibrium with solid S_1 in the system *W*–S_1; (3) the ternary saturation curve *DL* inside the prism, representing solutions in equilibrium, not only with solid S_1, but also with solid S_2, and (4) the ternary saturation curve *BL* inside the prism, representing solutions in equilibrium, not only with solid S_1, but also with ice. The phase theory defines nothing concerning the shape of such a saturation surface, it merely indicates the limits of its existence.

The surface *FDLE* is the saturation surface of solid S_2, being bounded by the four saturation curves (the two binary curves *FD* and *FE*, and the two ternary curves *DL* and *EL*) which represent solutions saturated with S_2. Every solution represented on this surface is a solution which is in equilibrium with solid S_2.

Lastly, we have the saturation surface *ABLE* every point of which represents a solution in equilibrium with ice. It is also bounded by four saturation curves, the two binary curves *AB* and *AE*, and the two ternary curves *BL* and *EL*.

We will summarise the results which we have so far obtained. We find represented in the space figure:

1. Three saturation *surfaces*, each depicting solutions saturated with one solid.

CDLB is the saturation surface of solid S_1,
FDLE ,, ,, ,, ,, S_2,
ABLE ,, ,, ,, ,, Ice.

2. Three polythermal saturation *curves*, each depicting solutions saturated with two solids.

These curves are formed by the intersection in pairs, of the three surfaces, and they represent solutions saturated with the two solids the saturation surfaces of which intersect in these curves.

BL is the saturation curve of solid S_1 + Ice,
EL ,, ,, ,, ,, S_2 + Ice,
DL ,, ,, ,, ,, S_1 + solid S_2.

3. One system invariant *point L*, depicting the solution saturated with the three solids $S_1 + S_2 +$ Ice.

All saturation surfaces and saturation curves meet in this point.

We have now to consider the isothermal sections of the space figure. Between the temperatures corresponding with the eutectic points L and E, a horizontal section of the figure will clearly cut each saturation surface along a curve, and each ternary saturation curve in a point; the three points thus obtained will be situated at the intersections by pairs of the three curves.

The section will cut no binary saturation curve.

The isotherm ($E_1B_2D_4$, Fig. 41) for any temperature within this range will therefore consist of three isothermal saturation curves (that of S_1, that of S_2 and that of ice), and three isothermal invariant points formed by the intersection of these curves in pairs, within the triangular section. This is the type which we have already characterised and represented in Fig. 34.

Between the temperatures corresponding with the eutectic points E and B, an isothermal section will still cut all three saturation surfaces, each along a particular curve. It will also cut the ternary saturation curves BL and DL, but not the curve EL, since we are outside its temperature range. The side of this isothermal section will cut the two binary saturation curves in the system W–S_2. The isotherm ($A_3B_1D_3F_4$, Fig. 41) within this range of temperature will therefore consist of three isothermal saturation curves with S_1, S_2, and ice respectively as solid phases, and two isothermal invariant points with S_1+ ice and S_1+S_2 as solid phases. The saturation curves of ice and of S_2 will extend to the side of the triangle, and terminate there in points representing two binary saturated solutions. This is the type represented in Fig. 32.

Between the temperatures corresponding with the eutectic point B and the melting point A an isothermal section will cut the three saturation surfaces, but only one ternary saturation curve DL. It will, however, cut both binary saturation curves in the system W–S_2, and both binary saturation curves in the system W–S_1. The isotherm (A_1A_2–$C_4D_2F_3$, Fig. 41) will then consist of three isothermal saturation curves with S_1, S_2, and ice as solid phases, and one isothermal invariant point with S_1+S_2 as solid phases. The saturation curves will terminate on one side of the triangle, in two points which represent binary solutions saturated with ice and S_2 respectively, and on another side of the triangle, in two points which represent binary solutions saturated with ice and S_1 respectively. This is the isothermal type represented in Fig. 29.

The most persistent isothermal type will be that given by sections of the space figure between the temperatures corresponding with the melting point A and the eutectic point D, for this will be, in nearly all cases, a very wide range—from 0° to the eutectic point of the fused salts. The isothermal section will now no longer cut the saturation surface of ice. It will cut only the saturation surfaces of S_1 and S_2, the binary saturation curve of S_1 in the system W–S_1, and of S_2 in the system W–S_2, and the ternary saturation curve of $S_1 + S_2$.

The isotherm ($C_3D_1F_2$, Fig. 41) will consist, therefore, of two isothermal saturation curves with S_1 and S_2 respectively as solid phases, and one isothermal invariant point with $S_1 + S_2$ as solid phases; the saturation curves will terminate on the sides of the triangle in points representing binary saturated solutions. This is the simple type which we considered at the beginning of this chapter.

Above the temperature of the eutectic point D, and below that of the melting point F, an isothermal section will still cut both the saturation surface of S_1 and that of S_2, but it will cut no ternary saturation curve; it will, however, again cut four binary saturation curves. The isotherm (C_2C_5–F_1F_5, Fig. 41) will therefore consist simply of the saturation curves of S_1 and of S_2, which will not intersect, but which will terminate at each end in points on the sides of the triangle, representing binary saturated solutions. This is the type shown in Fig. 37.

Finally, between the temperatures corresponding with the melting points F and C, an isothermal section will cut only the saturation surface of S_1, and the two binary saturation curves representing solutions in equilibrium with this salt as a solid phase. The isotherm (C_1C_6, Fig. 41) will consist, accordingly, of one saturation curve—that of S_1—terminated at each end in a point on the side of the triangle, representing a binary saturated solution. This is the type shown in Fig. 38.

The reader can easily convince himself that the transition types are obtained by sections of the space figure through the seven eutectic or melting points L, E, B, A, D, F, and C.

In order to complete our discussion of the space figure, we must investigate the significance of points which lie neither on saturation surfaces nor on saturation curves. Let us consider an isothermal saturation curve such as C_3D_1, on the saturation surface of solid S_1. It represents solutions which are in equilibrium, at this particular temperature, with solid S_1, and every point on it may therefore be joined by a conjugation line to the point S'_1, which represents solid S_1 at this temperature. The area $S'_1C_3D_1$ then depicts all possible phase complexes of solid S_1 and a solution on the saturation curve C_3D_1, at the temperature of the isotherm. It is clear that as the saturation curve C_3D_1 moves up and down the saturation surface, this complex area will generate a corresponding complex space, and that points inside this space represent complexes of solid S_1 and a solution on the saturation surface $CDLB$.

In the same way, every point on the saturation surface $FDLE$ may be joined by a conjugation line to a point on the edge S_2T representing pure S_2 at the same temperature, and a space will thus be generated every point of which represents a complex of solid S_2 and a solution on the saturation surface. Every point on the saturation surface $ABLE$ may be joined to a point on the line WT representing pure ice at the same temperature, and a third complex space will thus be formed.

Returning again to the isotherm $C_3D_1F_2$, we have seen that the solution represented by D_1 is in equilibrium with both S_1 and S_2 at this temperature, and, therefore, that conjugation lines may be drawn joining D_1 to every point on the line $S'_1S'_2$.

Points in the triangular area $S'_1D_1S'_2$ represent, then, complexes of solid S_1, solid S_2, and solution D_1 in this isotherm, and as the isothermal invariant point D_1 moves up and down the ternary saturation curve DL, so the area $S'_1D_1S'_2$ will generate a space every point of which represents a complex of solid S_1, solid S_2, and a solution at the same temperature, represented on the saturation curve DL. There will clearly be two other complex spaces which are generated in a similar manner. The points in one of these spaces will represent complexes of ice, solid S_1, and a solution represented on the ternary saturation curve *BL*, and those in the other, complexes of ice, solid S_2, and a solution represented on the saturation curve *EL*. Points in the horizontal plane containing *L* represent, as we have already seen, complexes of one, two, or all of the solid phases S_1, S_2, and ice, with the solution *L* (§ 34).

The space inside the figure formed by the three saturation surfaces is the space of unsaturated solutions, since it is clearly generated by the isothermal area of unsaturated solution, when the temperature assumes successively all possible values. The melting point *C* of the salt S_1 is the highest temperature at which a solid phase can exist in the system, and every point in the prism above the horizontal plane which contains the point *C* must, therefore, also represent an unsaturated solution.

It is somewhat difficult to picture these various spaces in a plane drawing, such as Fig. 41, and a space model is a great aid to the understanding of the space representation. A careful consideration will show, however, that the eight spaces detailed above together comprise the whole of the interior of the prism.

§ 37. We have discussed two methods by which the polythermal relations in the ternary system can be represented. We may construct, either a series of isotherms at various temperatures, or a space figure, but both these methods leave something to be desired. The first method necessitates the construction of a large number of pictures, particularly in the case where binary or ternary compounds can be formed, whilst the construction of a space figure in these cases is cumbersome, and we are further handicapped by the necessity of depicting this space figure in the plane of the paper. Several methods have been devised for representing the polythermal relations in the ternary system by means of a plane figure. It is clear that one such figure cannot give us complete information about all the variable factors in the way that the space figure does. In order to represent the conditions of equilibrium in the condensed ternary system by means of a plane figure, we have seen that it is necessary either to fix or to disregard one of the possible varying factors. For example, we commenced our discussion of the ternary system by considering the compositions of solutions saturated at a fixed temperature, and by so doing we reduced the variability of the system. Unsaturated solutions were depicted by an *area* in the isotherm, by a *space* in the polytherm; solutions saturated with one solid were depicted by a saturation *curve* in the isotherm, by a saturation *surface* in the polytherm, and solutions saturated with two solids were depicted in the isotherm by an invariant *point*, in the polytherm by a saturation *curve*.

All the methods which are used for representing the polythermal relations in the ternary system by means of a plane figure can be considered as projections upon a plane surface, of the space figure shown in Fig. 41. If, for example, the space figure is projected perpendicularly downwards upon the base WS_1S_2 of the prism, the picture shown in Fig. 42 is obtained. The binary eutectic point B (Fig. 41) projects into the point b, perpendicularly below it, upon the side WS_1 of the triangle (Fig. 42). The binary eutectic points E and D (Fig. 41) project similarly into the points e and d on the sides WS_2 and S_1S_2 respectively (Fig. 42). The ternary eutectic point L (Fig. 41) projects into a point l within the triangle (Fig. 42), the three polythermal saturation curves BL, EL, and DL (Fig. 41) project into the curves bl, el, and dl (Fig. 42), and the saturation surfaces of ice, S_1 and S_2 in Fig. 41 clearly project into the areas $Wble$, S_1bld, and S_2dle, respectively, of Fig. 42. These areas are marked in the figure with the corresponding solid phases, and points on a given saturation curve represent solutions saturated with the two solid phases the saturation areas of which are bounded by that curve; thus it is easy to see from the figure that the curve bl is the saturation curve of Ice + S_1, since the saturation areas of ice and of S_1 are separated by this curve.

The projection shows the essential features of the space figure itself; it shows the three saturation surfaces intersecting by pairs in the polythermal saturation curves, and it shows the ternary eutectic point as the point in which these three saturation surfaces and three saturation curves intersect. Fig. 42 does not, however, give the complete information yielded by the space figure, and it must be borne in mind that the temperature varies from point to point in the picture; although the actual value of the temperature corresponding with any given point is not expressed by Fig. 42, the latter is a polytherm and not an isotherm. Every point on a saturation curve represents, not a solution saturated with one solid at a fixed temperature as in the isotherm, but a solution saturated with two solids at a temperature the value of which is not expressed. The terminal point of a saturation curve on a side of the triangle represents, not a binary solution saturated with one solid at an arbitrarily fixed temperature as in the isotherm, but a binary invariant solution saturated with two solids at a definite eutectic temperature the value of which is not expressed. Since, however, the temperature corresponding with points on the saturation curves rises continuously from the ternary eutectic point *l*, and reaches its maxima in the binary eutectic points *b*, *d*, and *e*, the direction of the temperature change on these curves can be shown, and it is indicated in Fig. 42 by the arrow-heads, which point in the direction of rising temperature. The isothermal saturation curves lie, as we have seen, on the saturation surfaces, and they would be found in Fig. 42 by joining the points which represent solutions saturated with the same solid, at one and the same temperature. Some of the isothermal types are represented by dotted lines in this figure.

We see that the incompleteness of the polythermal representation given in Fig. 42 lies in the fact that, although the temperature varies from point to point, its value at any point does not receive actual graphical expression. The compositions of solutions are, however, completely and correctly represented; for example, the point *l* gives the true composition of the ternary eutectic solution. This point is the projection of the point *L* in the space figure, and since the projection was constructed by means of perpendicular lines parallel to the temperature axis, the position of the point *l* in the triangle WS_1S_2 is the same as the position of the point *L* in that horizontal triangular section of the space figure which contains it.

The meaning of a point in the plane projection is, to a certain extent, ambiguous. Let us consider, for example, the point *G*, which lies on the saturation curve *dl* in Fig. 42, and is the perpendicular projection of a corresponding point on the saturation curve *DL* in the space figure. The point *G* must also be the projection of every other point on the perpendicular line which passes through it, and since this line traverses a number of complex spaces, the point represents at one and the same time, not only a saturated solution, but also a number of phase complexes at a great variety of temperatures; the point corresponds with one definite temperature only when it is considered as the projection of a point on a saturation curve. In order, therefore, to remove this ambiguity, we shall consider a point in Fig. 42 to represent one phase only, namely, a solution which is saturated with one, two, or three solids, according to whether it lies in one of the areas, on one of the curves, or at the eutectic point; the complex spaces and the space of unsaturated solutions will receive no graphical representation in the plane projection.

This projection of the ternary polytherm is the one which is generally used by Schreinemakers, and we shall return to it later (Chapter V).

§ 38. We will now suppose that the space figure (Fig. 41) is projected, not upon the base, but upon the front vertical face TS_1S_2 of the prism, by means of lines which are *parallel* to the plane of the base, and which all radiate from points on the water axis *WT*. If, for example, we wish to construct the projection of the binary eutectic point *B* in Fig. 41, we must choose a point on the line *WT* at the same height above the base as the point *B*; we must join this point by a straight line to the point *B* and continue the line until it intersects the front face of the prism. The point of intersection will clearly lie on the boundary line S_1T, and it is given by the point *b* in Fig. 43, which represents this projection. The binary eutectic point *E* (Fig. 41), projected in the same way, by means of a line which passes through a point on the axis *WT* and is parallel to the plane of the base, will clearly give a point such as *e*, which lies on the side S_2T in Fig. 43. When the ternary eutectic point *L* is projected by means of a line which passes through the axis *WT*, its projection will be given by a point such as *l*, which lies within the rectangle in Fig. 43. The binary saturation curves *CD* and *FD*, and the eutectic point *D* in the binary system S_1–S_2, since they already lie on the front face of the prism, will appear unchanged in Fig. 43. The three ternary saturation curves, which rise from the ternary eutectic point and end in the three binary eutectic points, are given by *lb*, *le*, and *ld* in this figure, and the saturation surfaces of S_1 and S_2

by the areas *cdlb* and *fdle*, which are marked with the corresponding solid phases. An examination of Fig. 41 will show that the projection of the ice saturation surface upon the front face of the prism will be superimposed upon the projections of the saturation surfaces of S_1 and S_2, and if, therefore, the points of Fig. 43 are to be free from ambiguity, we must consider this figure as giving only the polythermal saturation curves and the saturation surfaces of S_1 and S_2; the saturation surface of ice, the space of unsaturated solutions, and the complex spaces can receive no graphical representation in this plane projection.

Since the points in the space figure have been projected in a direction parallel to the base, their height above the base remains unchanged, and the temperature corresponding with a point in Fig. 43 is therefore correctly measured by the distance of the point above the line S_1S_2, in a direction parallel to S_1T or S_2T. The compositions of solutions are, however, not completely represented by the points in this figure. Let us consider, for example, the point D_1 of Fig. 41, which lies on the saturation curve LD, and in the horizontal triangular section $W'S'_1S'_2$. The projection of this point will be given by the intersection of the straight line $W'D_1$ with that side $S'_1S'_2$ of the triangular section which lies on the front face of the prism. Now we have shown that all points on a line such as $W'D_1$ represent mixtures which contain the same proportion of the two salts S_1 and S_2. The projection of the point D_1 will give, therefore, the correct proportion of the two salts contained in the saturated solution represented by D_1. Since, however, the percentage of water in the solution D_1 is measured by the distance of the point D_1 from the face of the prism opposite to the axis WT, and since we have projected the point upon this face, the projected point will give no information about the water content of the solution which it represents. We see that a point in the plane projection of Fig. 43 represents the true temperatures of a solution, and the correct percentage composition of the *salt mixture* contained in that solution, but the water content is undefined; to every point in Fig. 43 there corresponds a certain unexpressed value for the water content of the solution which it represents, and this value varies from point to point.

We can construct the polythermal representation given in

Fig. 43 without reference to the space figure. For this purpose, the composition of the liquid phase must be expressed in a different form from that hitherto employed. Instead, namely, of referring the weight of each component to a total weight of 100 parts of solution, we shall refer the weight of each component to 100 parts by weight of the total salts $S_1 + S_2$. Suppose a ternary solution containing W, S_1, and S_2 has a total salt content of 100 grams, and let x be the weight of the salt S_1 in this solution. The weight of the salt S_2 will then be $100 - x$, and the remainder of the solution, which we will call y grams, will give the weight of water present in this phase. We can then express its composition in the following form:

$$yW, xS_1, \overline{100 - x}S_2,$$

and in this form the concentrations of the two salts are so arranged that their sum is constant and equal to 100. If, therefore, a point on the concentration axis S_1S_2 of Fig. 43 divides this axis into two sections, such that the length of one section gives the concentration x of the salt S_1 in a liquid phase, then the length $100 - x$, of the other section, gives the concentration of the salt S_2 in that phase. The variations of x (and therefore of $100 - x$) with the temperature T can then be represented by points inside a rectangle such as TS_1S_2 of Fig. 43, and the picture will show the effect of temperature change upon the percentage composition of the salt mixture contained in the liquid phase; the water content y of these phases will vary from point to point, and the actual value at a given point will not find expression in the picture. We shall, in fact, obtain the same figure as would be given by a projection of the space figure (Fig. 41) upon the front face of the prism in the way which we have described.

It can be seen that this method of representing the polythermal relations in the ternary system resembles the method used for the binary system. Points on the axis S_1T between b and c represent saturated aqueous solutions of pure S_1 at various temperatures, instead of pure S_1 itself as in the binary polytherm; such points correspond, namely, with 100 per cent. S_1 referred to the total salt content, and not to the total weight, of the mixtures which they represent. In the same way, a point between e and f on the axis S_2T represents a saturated aqueous solution of pure S_2 at a certain temperature, and a point on one of the saturation curves or surfaces within the rectangle, a saturated aqueous solution of a mixture of S_1 and S_2 in a proportion which can be directly measured from the figure. It must be remembered that, in order to remove all ambiguity, we have decided to leave the saturation surface of ice and the complex spaces unconsidered. Fig. 43 differs further from the binary polytherm, in that the curves lb, ld, and le, being polythermal saturation curves in a ternary system, represent the compositions of solutions saturated at various temperatures with two solid phases. We have already pointed out that the curves de and df are binary saturation curves representing the compositions of solutions saturated with one solid, and the point d is a binary eutectic point. It is important to remember this, since the fact is not at once evident from the figure. The binary system S_1–S_2 is alone *completely* represented by Fig. 43, since in this system the water content is constant and actually equal to zero ; the fact that the figure fails to express the value of the water content of liquid phases is immaterial in the case of the anhydrous system.

An isotherm is represented in Fig. 43 by a line parallel to S_1S_2, every point of which represents, therefore, a solution at one and the same temperature. It can be seen clearly that such a line, between the temperatures of the points e and l, will cut all three polythermal saturation curves. These isotherms will therefore show three isothermal invariant points.

The point in which the line of constant temperature cuts the curve bl will give the composition of the salt mixture contained in the isothermal invariant solution saturated with ice and solid S_1 ; that in which it cuts the curve dl will give the composition of the salt mixture contained in the isothermal invariant solution which is saturated with the two salts, and that in which it cuts the curve el, the composition of the salt mixture in the isothermal invariant solution saturated with ice and solid S_2. Between the temperatures of the points b and e, a constant temperature line will cut only two saturation curves ; between those of the points d and b only one, and above the temperature of the point d, no ternary saturation curve. The corresponding isotherms will therefore show two, one, and no ternary isothermal invariant points. We do not need to consider this case further, since it can only lead us to the isothermal types which we have already deduced.

The method of representation described in this paragraph was introduced by Jänecke, and we shall use it to investigate the polythermal conditions of equilibrium in the ternary system when a compound can occur as a solid phase.

§ 39. We will suppose that the two simple salts S_1 and S_2 can unite to form an anhydrous double salt D. There are then four solid phases which can occur in the condensed ternary system, namely, ice, S_1, S_2, D, and the possibility arises that more than one invariant equilibrium may exist in the system. We might conceivably have either of the following solid phase triads in equilibrium with solution at a system invariant point:

Ice + S_1 + D + Solution . . . 1.
Ice + S_2 + D + Solution . . . 2.
Ice + S_1 + S_2 + Solution . . . 3.
S_1 + S_2 + D + Solution . . . 4.

We will consider first the invariant equilibrium No. 4, which occurs when the two simple salts and the double salt coexist in contact with an invariant solution, and we will determine the phase reactions which occur when heat is added to, or withdrawn from, the system in invariant equilibrium; those reactions must be such as to leave the composition of the liquid phase unaltered. Now since no one of the three solid phases S_1, S_2, and D contains water, it is clear that the separation or dissolution by the liquid phase of one, two, or all of these solids in any proportion must increase or decrease the concentration of water in the liquid phase, and hence that the invariant phase reactions must involve the solid phases only, the liquid phase taking no part in them. The reactions are therefore:

$$S_1 + S_2 \rightarrow D,$$

and

$$D \rightarrow S_1 + S_2.$$

They consist in the union of the two simple salts with the formation of the double salt, and in the decomposition of the double salt with the formation of the two simple salts; since

Figs. 44, 45, 46.

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these reactions take place only between the solid phases, it is clear that they will leave the composition of the liquid phase unchanged. Of the two opposing phase reactions given above, one must occur when heat is added to, and the other when heat is withdrawn from, the invariant system in equilibrium. If the double salt is stable at temperatures above that which corresponds with this invariant system, it will be formed from the two simple salts when heat is added, and decomposed into these two when heat is withdrawn. The phase reactions in equilibrium at the invariant point will then be given by the following notation:

$$S_1 + S_2 \rightleftarrows D \quad . \quad . \quad . \quad . \quad 5.$$

where, following our custom, we denote the reaction which occurs on the addition of heat by the upper arrow, and that which occurs on the withdrawal of heat by the lower arrow. If, on the other hand, the double salt is stable at temperatures below that which corresponds with the invariant system, it will be decomposed into the two simple salts when heat is added, and formed from them when heat is withdrawn. The phase reactions in equilibrium at the invariant point will then be given by the following notation:

$$D \rightleftarrows S_1 + S_2 \quad . \quad . \quad . \quad . \quad 6.$$

Both cases are possible, and we will suppose first that the relations are those represented by the notation 5.

The addition of heat to the invariant system will then result in the following phase reaction:

$$S_1 + S_2 \rightarrow D.$$

The system will gain a degree of freedom when one of the solid phases S_1 or S_2 has been removed during the course of this reaction. The two following monovariant systems can therefore exist at temperatures above that of the invariant point:

$$S_1 + D + \text{Solution}^1 \quad . \quad . \quad . \quad . \quad 7.$$
$$S_2 + D + \text{Solution} \quad . \quad . \quad . \quad . \quad 8.$$

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[1] Although the liquid phase takes no part in the equilibrium reactions, the presence of this fourth phase is essential to the existence of a *ternary* invariant system.

The removal of heat from the invariant system will result in the opposing reaction:

$$D \rightarrow S_1 + S_2.$$

The solid double salt is the only phase which can be consumed by this reaction, and the only monovariant system which can exist at temperatures below that of the invariant point is:

$$S_1 + S_2 + \text{Solution} \quad . \quad . \quad . \quad . \quad . \quad 9.$$

The ternary system W–S_1–S_2 is represented, in this case, by Jänecke's method, in Fig. 44. The point M is the system invariant point representing the conditions of equilibrium in the invariant system, S_1–S_2–D–Solution, and it gives the temperature of the invariant equilibrium, and the composition of the salt mixture contained in the invariant solution; the water content of this solution is not expressed by the figure. The two monovariant systems shown above (Nos. 7 and 8) can exist at temperatures above that of the invariant equilibrium, and from the system invariant point M the two corresponding polythermal saturation curves must diverge in the direction of rising temperature.

The curve MB, corresponding with the monovariant system No. 7, is the saturation curve of the two solids $S_1 + D$, whilst the curve MC, corresponding with the monovariant system No. 8, is the saturation curve of the two solids $S_2 + D$; these curves reach their temperature maxima in the binary eutectic points which represent solutions also in equilibrium with these salt pairs. Since, namely, the double salt is stable at temperatures above that of the point M, it will be a possible solid phase in the binary system S_1–S_2, which will then no longer show the simple relations previously assumed for it. It must show, as in Fig. 44, three saturation curves AB, BC, and CK representing liquid phases in equilibrium with the solids S_1, D, and S_2 respectively. The binary saturation curves of S_1 and of D intersect in the binary invariant point B, which represents a liquid phase in equilibrium with $S_1 + D$, and forms the end point of the ternary saturation curve also representing solutions in equilibrium with these two solid phases. Similarly, the point C is the binary invariant point at which the two solids $S_2 + D$ are in invariant equilibrium with a liquid phase, and this point is, therefore, the end point of the ternary saturation curve of $S_2 + D$.

The monovariant system No. 9 can exist at temperatures below that of the system invariant point M, and a corresponding saturation curve diverges, therefore, from this point in the direction of falling temperature. The curve MG is the saturation curve of $S_1 + S_2$, and its range of existence is bounded on the side of low temperatures, by the appearance of ice as a third solid phase, and the formation of a second system in invariant equilibrium (No. 3). The point G in Fig. 44 is the system invariant point at which the three solid phases $S_1 + S_2 +$ Ice are in equilibrium with an invariant solution, and the phase reactions occurring at this point when heat is added or withdrawn must clearly be represented by the following notation :

$$\text{Ice} + S_1 + S_2 \rightleftarrows \text{Solution } G.$$

The three solids will be dissolved or separated by the solution G in the same proportion as that in which it contains them, and its composition will be kept constant in this way. It is clear that the point G is a ternary eutectic point, and that the three following monovariant systems all exist at temperature above that with which it corresponds :

$S_1 + S_2 +$ Solution . . . . 9.
Ice $+ S_1 +$ Solution . . . . 10.
Ice $+ S_2 +$ Solution . . . . 11.

The corresponding polythermal saturation curves diverge from the point G in Fig. 44. The curve GM, corresponding with the monovariant system No. 9, is the saturation curve of $S_1 + S_2$ which we have just discussed, and its other terminal point is the system invariant point M. The curve GF, corresponding with the monovariant system No. 10, is the saturation curve of Ice $+ S_1$, and it reaches its temperature maximum at the eutectic point F in the binary system W–S_1. The curve GH is the saturation curve of Ice $+ S_2$, and it reaches its temperature maximum at the eutectic point H in the binary system W–S_2.

It can be seen that the system invariant point M, unlike G, is not a eutectic point. It is not a lower temperature limit to the existence of the liquid phase, since the saturation curves do not all diverge from it in the direction of rising temperature, as is the case with the eutectic point G; it is, according to the definition given in § 17, a ternary transition point. The saturation surfaces, which represent solutions saturated with one solid only, are marked in Fig. 44 with their corresponding solid phases. It can be seen that the three saturation surfaces of S_1, S_2, and D all meet in the point M, which represents a solution saturated with all three salts, and that the temperature of this point is the lowest at which the double salt can exist in equilibrium with a liquid phase. The point M is therefore said to be the transition point of the double salt; below the transition temperature the two simple salts can coexist in equilibrium with solutions, whilst above it they must unite to form the double salt.

§ 40. We must now investigate the second of the two cases distinguished in the previous chapter, namely, that in which the phase reactions in equilibrium at the invariant point $S_1 + S_2 + D$ + Solution, are represented by the notation:

$$D \rightleftarrows S_1 + S_2.$$

The addition of heat to the invariant system will then result in the decomposition of the double salt, and the only monovariant system which can exist at temperatures above that of the invariant point is the following:

$$S_1 + S_2 + \text{Solution.}$$

The withdrawal of heat from the invariant system will cause the formation of the double salt, and the two following monovariant systems will exist at temperatures below that of the invariant point:

$$S_1 + D + \text{Solution,}$$
$$S_2 + D + \text{Solution.}$$

This case is represented in Fig. 45, where the point M, again a transition point, represents the invariant solution in equilibrium with the three salts $S_1 + S_2 + D$. The saturation curve of $S_1 + S_2$ now diverges from the point M in the direction of rising temperature, and it ends in the eutectic point E, which represents the invariant solution in equilibrium with these two solids in the binary system S_1–S_2. Since, namely, the double salt cannot exist, in the case we are considering, above the temperature of the transition point *M*, this system is of the simplest type, and shows only the saturation curves *AE* and *KE* of the component salts, and the single eutectic point *E*.

The saturation curves of $S_1 + D$ and of $S_2 + D$ diverge from the transition point in the direction of falling temperature. The curve *MR* is the saturation curve of $S_1 + D$, the curve *ML* that of $S_2 + D$, and both these curves are bounded on the side of low temperatures by the appearance of ice as a third solid phase, and the formation of a system in invariant equilibrium. (Nos. 1 and 2 of the previous paragraph.) The point *R* of Fig. 45 represents the invariant solution in equilibrium with the three solid phases Ice $+ S_1 + D$, the point *L* that in equilibrium with the three solid phases Ice $+ S_2 + D$, and both these points are represented in Fig. 45 as eutectic points. The phase reactions in equilibrium at the eutectic point *R* are:

$$\text{Ice} + S_1 + D \rightleftarrows \text{Solution } R,$$

and those in equilibrium at the point *L*:

$$\text{Ice} + S_2 + D \rightleftarrows \text{Solution } L.$$

Corresponding with the three monovariant systems which can exist at temperatures above that of the eutectic point *R*, three saturation curves must diverge from this point in the direction of rising temperature. They are the saturation curves of S_1+D, of Ice $+ S_1$, and of Ice $+ D$. The saturation curve *RM*, of $S_1 + D$, is bounded on the side of high temperature by the transition point *M*, as we have already seen. The saturation curve *RF*, of Ice $+ S_1$, reaches its temperature maximum at the corresponding eutectic point *F* in the binary system W–S_1. The third curve *RP*, which diverges from the point *R*, is the saturation curve of Ice $+ D$. The three saturation curves which diverge from the second eutectic point *L* represent the compositions of solutions in the three following monovariant systems:

$S_2 + D +$ Solution,
Ice $+ S_2 +$ Solution,
Ice $+ D +$ Solution.

The curve *LM* is the saturation curve of $S_2 + D$, which ends in the transition point *M*. The curve *LH* is the saturation curve of Ice $+ S_2$, and it reaches its temperature maximum at the eutectic point *H* in the binary system W–S_2. The curve *LP* is the saturation curve of Ice $+ D$, and we have already seen that this saturation curve diverges also from the eutectic point *R* in the direction of rising temperature. It follows that the two ternary eutectic points *R* and *L* are joined by a continuous saturation curve, that of Ice $+ D$, which diverges from both in the direction of rising temperature, and attains, therefore, a temperature maximum at a point between them; we shall consider later the significance of this temperature maximum.

It is clear from Fig. 45 that the transition point *M* represents, in this case, the highest temperature at which the double salt can exist in equilibrium with a liquid phase, and we see that the invariant equilibrium denoted by No. 4 in the previous paragraph is actually realised when the range of existence of the double salt is limited within the temperature interval in which saturated solutions can exist; this invariant equilibrium then occurs at the transition point of the double salt. If the transition point is a lower temperature limit to the existence of the double salt, as in Fig. 44, then the equilibrium No. 3 is also realised. If, on the other hand, the transition point is an upper temperature limit to the existence of the double salt, as in Fig. 45, then the two invariant equilibria Nos. 1 and 2 are realised, but not No. 3.

§ 41. There is a third possibility, since the double salt may be stable through the whole range of temperature within which saturated solutions can exist. In this case, which is represented graphically in Fig. 46, solid S_1 can never exist in stable contact with solid S_2; they must unite at all temperatures to form the double salt, and the saturation surfaces of S_1 and of S_2 will be entirely separated from each other by that of the double salt, as shown in the figure. The double salt will be capable of existence, both in equilibrium with fused salt mixtures in the anhydrous system S_1–S_2, as represented by the curve *BC*, and in equilibrium with ice and ternary solutions in the system W–S_1–S_2, as represented by the curve *RL*. The binary system S_1–S_2 may then show two eutectic points B and C representing binary solutions saturated with :

$$S_1 + D,$$

and

$$S_2 + D \text{ respectively,}$$

and the ternary system may show two eutectic points R and L, representing ternary solutions saturated with :

$$S_1 + D + \text{Ice},$$

and

$$S_2 + D + \text{Ice respectively.}$$

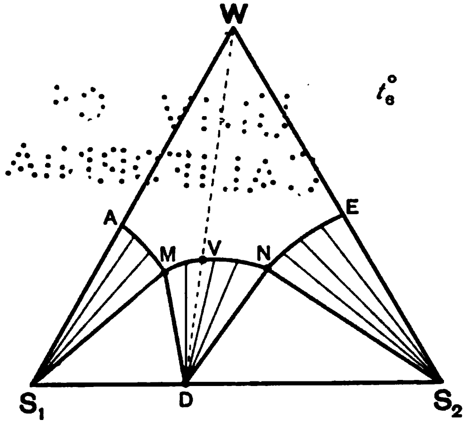
Three ternary saturation curves will diverge from the eutectic point R. The saturation curve RB, of $S_1 + D$, will end in the binary eutectic point B, the saturation curve RF, of S_1 + Ice, in the binary eutectic point F, while the saturation curve RPL, of D + Ice, must diverge in the direction of rising temperature from both eutectic points R and L, as it did in the case represented by Fig. 45 of the previous paragraph ; it therefore passes through a temperature maximum.

Of the other two saturation curves which diverge from the eutectic point L, LC is the saturation curve of $S_2 + D$, ending in the binary eutectic point C, and LH is the saturation curve of S_2 + Ice, ending in the binary eutectic point H.

The point D, on the side S_1S_2 of the rectangle in Fig. 46, represents the percentage composition of the double salt itself, and points on the dotted line DQ, where it traverses a saturation surface or intersects a saturation curve, represent, therefore, saturated solutions which contain the two simple salts in the same proportion as does the double salt itself, and the compositions of which can thus be expressed in terms of W and D alone. Now it is seen that the dotted line traverses only the ternary saturation surface of the double salt, and intersects only the binary saturation curve BC of this salt, and the ternary saturation curve RL of this salt and ice. It follows that the compositions of all solid phases in equilibrium with solutions which are represented by points on the dotted line can also be expressed in terms of water and the double salt alone, and, therefore, that every point on this line represents a saturated solution in a system of a lower order than the third. Thus the point Q represents the solid double salt in equilibrium with a liquid salt mixture of the same composition as the double salt; it is, therefore, the melting point of the double salt in the unary system D. Points between Q and P represent saturated aqueous solutions which contain the simple salts in the same proportion as does the double salt, and are in equilibrium with solid double salt; they represent, in other words, solutions saturated with the double salt, at various temperatures in the *binary* system W–D. The point P is the eutectic point in this binary system, since it represents a solution, containing only W and D, in equilibrium with Ice + D.

We see that the section DQ, of the figure which gives the polythermal conditions of equilibrium in the ternary system W–S_1–S_2, represents in this case a system of the next lower order, namely, the binary system W–D (or the unary system D in the limiting case of the point Q where the water content is zero). This section divides the figure into two parts, which can be considered as giving the conditions of equilibrium in two ternary systems of the simplest type (*cf.* § 16). The system W–S_1–D is represented inside the rectangle AS_1DQ, and it can be compared with the simple system W–S_1–S_2, in which no compound occurs (Fig. 43). In the ternary system W–S_1–D, there occur only three polythermal saturation curves which diverge from the eutectic point R; and this point is the only ternary invariant point in the system. The curve RP is the saturation curve of Ice + D, and it must reach its temperature maximum in the binary eutectic point P, at which these two solid phases are in equilibrium with an invariant solution in the binary system W–D. The ternary system W–S_2–D is represented within the rectangle KS_2DQ, and it is also of the simplest type, showing only one eutectic point L, and three polythermal saturation curves. The curve, LP is the saturation curve of Ice + D in this system, and it must also reach its temperature maximum in the corresponding binary eutectic point P. We see now the significance of the temperature maximum in the continuous saturation curve RPL, of Ice + D. This ternary saturation curve reaches its maximum in a point which represents an invariant binary system, and not a monovariant ternary system, as do the other

VIII.



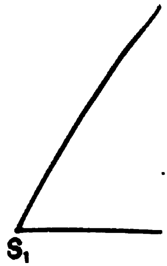
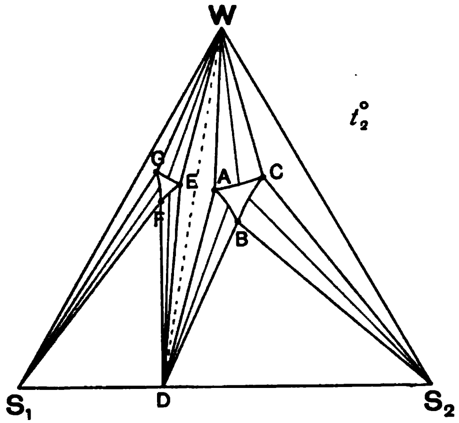


FIG. 47.



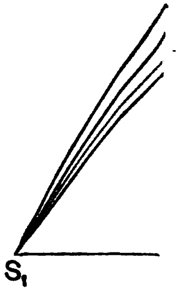
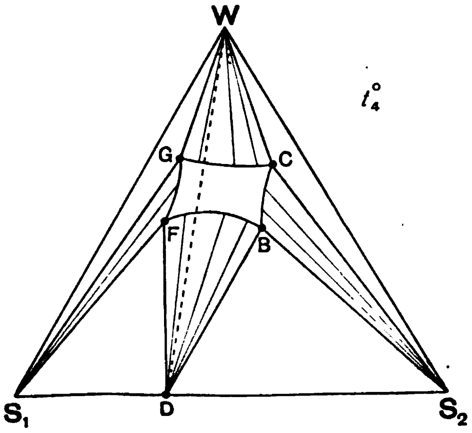


FIG. 49.



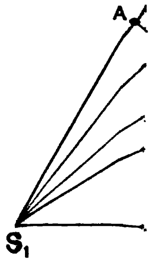


FIG. 51.

SHEET VIII.

points on it. The maximum represents, namely, the eutectic point in the binary system W–D, and it lies at the intersection of the line DQ with the ternary saturation curve of Ice + D.

§ 42. We are now in a position to discuss in more detail the various isothermal types which may occur in the system W–S_1–S_2 when a double salt can exist as a solid phase, and we shall suppose first that the system is represented by Fig. 46, the double salt being stable through the whole temperature range. We have seen that, in this case, the ternary system can be considered at every temperature as built up from two others, each of the simplest type. The most persistent isothermal type will be that which obtains at temperatures between the melting point of ice and the temperature of the eutectic point C in the anhydrous binary system S_1–S_2, since this will be, in nearly all cases, a very wide range of temperature. The isotherm at a temperature t_8, within this range, will be represented in Fig. 46 by a straight line parallel to the side S_1S_2, and at such a height above it as corresponds with the temperature t_8 on the chosen scale of measurement. It can be seen that this line traverses the saturation surfaces of S_1, D, and S_2 in order, and intersects the saturation curves of $S_1 + D$ and of $S_2 + D$. The isotherm at this temperature will therefore show the isothermal saturation curves of S_1, D, and S_2, and the isothermal invariant points formed by the intersections of these curves, and representing solutions saturated with $S_1 + D$, and $S_2 + D$. This isotherm is represented in Fig. 47, the points M and N on the polythermal saturation curves of $S_1 + D$ and $S_2 + D$ respectively in Fig. 46 reappearing here as isothermal invariant points; the compositions of the solutions which these points represent are *completely* defined by them in Fig. 47, whilst in Fig. 46 the points give only the compositions of the salt mixtures contained by these solutions. Now, since the system can be considered, *at all temperatures*, as built up from the two simpler ternary systems W–S_1–D and W–S_2–D, the line WD, in Fig. 47, must divide the isotherm into two parts which can be considered as giving the conditions of equilibrium, at the temperature t_8, in two systems of the simplest type. We saw, however, in §§ 29 and 30 that this can only be the case when the line WD intersects the saturation curve MN of the double salt, both isothermal invariant points representing congruently saturated solutions. The isotherm in the system W–S_1–D (Fig. 47) is represented within the triangle WS_1D, and the isotherm in the system W–S_2–D within the triangle WS_2D. We saw that the point V, in which the line WD intersects the saturation curve of D, represents the saturated solution of the double salt in the binary system W–D at the temperature of the isotherm; this point clearly corresponds with the point V of Fig. 46, at which the constant temperature line cuts the dotted line DQ, the points of which represent, not ternary, but binary saturated solutions.

The isothermal types which are derived from Fig. 46 at low temperatures show very clearly that the ternary system W–S_1–S_2 is built up, in the case that we are discussing, from two simpler systems which can be considered quite independently of each other. The constant temperature line t_1, in Fig. 46 lies just below the ternary eutectic point R in the system W–S_1–D, which is represented within the rectangle AS_1DQ. No saturation curves will therefore occur in the triangle WS_1D which forms parts of the ternary isotherm at this temperature (Fig. 48), since all points in it must represent completely solid complexes. In the system W–S_2–D, which is represented within the rectangle QDS_2K (Fig. 46), the constant temperature line intersects all three polythermal saturation curves, and the points of intersection reappear in the triangle WS_2D of the isotherm (Fig. 48) as three isothermal invariant points. The point A represents the solution in equilibrium with Ice + D at this temperature, the point C that in equilibrium with Ice + S_2, and the two points are joined by the saturation curve AC of ice; the point B represents the solution saturated at this temperature with $S_1 + D$, and it is joined to the point A by the saturation curve BA of the double salt, and to the point C by the saturation curve BC of the simple salt S_2. This isothermal type can be compared with that shown in Fig. 34, which we deduced for the ternary system of simplest type, at a temperature immediately above its eutectic point.

At the temperature t_2 the constant temperature line in Fig. 46 is seen to cut all three polythermal saturation curves in the system W–S_1–D, and all three in the system W–S_2–D. The isotherm at this temperature must, therefore, be of the form shown in Fig. 49; the isothermal type which occurred in the system W–S_2–D at the lower temperature t_1, and was represented in the triangle WS_2D, appears now in the system W–S_1–D also, and is represented in the triangle WS_1D. It is to be noticed here that both curves GE and AC represent solutions saturated with ice, both curves EF and AB solutions saturated with the double salt, while both the isothermal invariant points E and A represent solutions in equilibrium with Ice + D. It is in fact seen that the constant temperature line t_2 in Fig. 46 cuts the polythermal saturation curve RL of Ice + D in two points, and these points reappear as isothermal invariant points in Fig. 49. As the temperature rises above t_2, it can be seen from Fig. 46 that these two points, in which the constant temperature line cuts the saturation curve RL, will approach one another, and will finally coincide in the point P, which is the eutectic point in the binary system W–D. The two invariant points E and A in the isotherm (Fig. 49) will therefore approach one another as the temperature rises, and at the temperature t_3, of the eutectic point P, the isotherm will show the transition form of Fig. 50. The two invariant points E and A of Fig. 49 have here reached coincidence in the point P, which, since it represents the eutectic solution in the binary system W–D, lies on the line WD. There is now only one continuous isothermal saturation curve GC of ice, and one continuous saturation curve FB of the double salt, these two curves touching in the point P, which represents the only solution that can exist at this temperature in equilibrium with both ice and the double salt.

Fig. 46 shows that, at a temperature t_4, slightly above t_3, the constant temperature line no longer cuts the polythermal saturation curve of Ice + D, and therefore that no isothermal invariant solution can exist at this temperature in equilibrium with these two solid phases. The constant temperature line still cuts, however, the remaining four polythermal saturation curves, and the isothermal type is therefore given by Fig. 51. The two saturation curves of ice and of D, which touch at the eutectic temperature t_3, separate from each other at higher temperatures so that no point exists which is common to both, and which would represent a solution saturated with the two corresponding solids. A comparison with Fig. 38 will show that, in this isotherm also, the two systems represented within the triangles WS_1D and WS_2D both present an isothermal type which has already been deduced for the simplest ternary system.

A number of other isothermal types occur between that shown in Fig. 51 and the most persistent type, which we discussed first (Fig. 47). The deduction of these will be left to the reader; they can all be considered as combinations of simple types, owing to the fact that the two systems W–S_1–D and W–S_2–D can be treated independently of each other.

§ 43. We will now consider the isothermal types which may occur when the conditions of equilibrium in the system are represented by Fig. 45, *i.e.*, when the double salt has a transition point which forms an upper temperature limit to its existence in the system. Above the temperature t_2, of the transition point M, the only two solid phases which can occur are the two simple salts S_1 and S_2, and the isothermal types at temperatures above t_2 must therefore be identical with those which we have deduced for the simple system in the higher temperature ranges (§ 35). The point D represents, as before, the composition of the double salt, and points on the dotted line, where it traverses saturation surfaces or intersects saturation curves, represent saturated solutions which contain the two simple salts in the same proportion as does the double salt, and the composition of which can therefore be expressed in terms of W and D alone. Points on this line which lie between G and P represent saturated solutions in equilibrium with solid double salt, and since the ~~compositions of the liquid~~ phases represented by these points, and of the solid phase with which these liquids are in equilibrium, can be expressed in terms of W and D alone, such points must represent saturated solutions in the binary system W–D; the point P, which lies on the ternary saturation curve of Ice + D, must represent the eutectic point in this binary system. The same argument may be applied here, to show that the binary eutectic point P lies at the temperature maximum of the ternary saturation curve RL (Fig. 45), as we used for the similar case discussed in the previous paragraph, and represented in Fig. 46. It follows that the isothermal types for all temperatures up to that of the point G can be considered as combinations of two simpler types, and they must, in fact, be identical with those deduced in the previous paragraph for the case represented in Fig. 46. The isotherm at a temperature t_6

(Fig. 45), above the melting point of ice, is given for example by Fig. 47, in which the line *WD* intersects the saturation curve of the double salt, and thereby divides the figure into two simple isothermal types represented within the triangles WS_1D and WS_2D.

At a temperature above that of the point *G*, the dotted line traverses the saturation surface of the simple salt S_1, and points on it here represent solutions which contain the simple salts in the same proportion as does the double salt, but which are in equilibrium, not with the double salt itself, but with the simple salt S_1. The composition of this solid phase cannot be expressed in terms of *W* and *D* alone, and the system *W–D* ceases therefore to be a binary system as soon as the temperature rises above t_4, that of the point *G*. The isotherm at a temperature between t_4 and the transition temperature t_3 must still show three saturation curves, since a line of constant temperature within this range still intersects the three saturation surfaces of S_1, *D*, and S_2 in order, but it will no longer be possible to consider the isotherm as a combination of two simple types shown by the systems W–S_1–D and W–S_2–D. The isotherm at the temperature t_3 is represented in Fig. 52. Since a saturated solution containing the two simple salts in the same proportion as does the double salt is in equilibrium at this temperature with the salt S_1, the line *WD* of Fig. 52 intersects the isothermal saturation curve *AB* of S_1 and not that of the double salt; the point of intersection *N* clearly corresponds with the point *N* of Fig. 45, in which the constant temperature line cuts the dotted line. The isothermal type of Fig. 52 is the one which we have discussed in detail in § 30; it represents the case in which the double salt is decomposed by water, one of the isothermal invariant solutions being incongruently saturated, and we see now that this type occurs between the temperature of the point *G* and that of the transition point *M*.

The isothermal relations are very similar when the transition point forms a lower stability limit to the existence of the double salt, when, therefore, the conditions of equilibrium in the system are those represented by Fig. 44. The isothermal types at temperatures below that of the transition point *M* will now be identical with those which occur at the lower temperature ranges in the binary system of the simplest type (§ 34). At temperatures above that of the transition point the saturation curve of the double salt will also appear in the isotherm. Between the temperature t_2 and t_4 (Fig. 44) the dotted line PQ, the points of which represent saturated solutions containing the simpler salts in the same proportion as does the double salt, traverses the saturation surface of the simple salt S_1, and not that of the double salt. Within this temperature range the double salt is therefore decomposed by water, and the isothermal type is that of Fig. 52, in which the line WD intersects the saturation curve of S_1. At temperatures above t_4, the dotted line traverses the saturation surface of the double salt, and saturated solutions which can be formed by dissolving the double salt in water are therefore in equilibrium with solid double salt at these temperatures. The double salt is not then decomposed by water, and the isothermal type is that of Fig. 47, in which the line WD intersects the saturation curve of the double salt.

The range of temperature within which the double salt is capable of existing as a solid phase, in equilibrium with a solution, is called the "existence interval" of the double salt.

The existence interval can be resolved into other temperature intervals, each characterised by the particular behaviour which is observed when the double salt is brought into contact with water or ice. Thus the temperature range within which the double salt is dissolved by water or ice to form a saturated solution in equilibrium with solid double salt is called the "interval of pure solution," whilst that range within which the double salt is decomposed by water with the separation of one of the simple salts is called the "transition interval."

We see that when a double salt possesses a transition point it also possesses a transition interval within which it is decomposed by water. This interval lies in the neighbourhood of the transition temperature, and its extent, which depends partly upon the shape of the ternary saturation curves, cannot be predicted by the phase theory.

When the conditions of equilibrium in the system are represented by Fig. 44, the existence interval of the double salt extends from the temperature of the transition point M to the melting point Q of the pure double salt. This interval consists of a transition interval (t_2 to t_4), and an interval of pure solution (t_4 to the melting point Q). When the conditions of equilibrium in the system are represented by Fig. 45, the existence interval of the double salt extends from the temperature of the lower eutectic point L to that of the transition point M. Since, however, the point P is the eutectic point in the binary system W–D, only solid complexes of Ice + D can exist in the system at temperatures below it, and therefore a mixture of ice and double salt represented by a point on the dotted line below P will remain unchanged. The double salt will neither be decomposed nor dissolved, and the range of temperature which extends from that of the ternary eutectic point L to that of the binary eutectic point P is therefore called the "indifferent interval." Since the double salt can still exist at these temperatures in equilibrium with ternary solutions (as shown by the saturation surface of D, which extends to the eutectic point L), the indifferent interval forms a part of the existence interval of the double salt. The interval of pure solution extends, in the case represented by Fig. 45, from the temperature of the binary eutectic point P to the temperature t_4, and the transition interval from the temperature t_4 to the transition temperature t_2. We see that the existence interval can, in this case, be resolved into three other intervals: the indifferent interval, the interval of pure solution, and the transition interval.

Finally, if the conditions of equilibrium in the system are represented by Fig. 46, there exists no transition interval, since saturated solutions formed by dissolving the double salt in water are in equilibrium at all temperatures with solid double salt. The existence interval extends from the lower eutectic point L to the melting point Q of the pure double salt, and it consists of an indifferent interval (from the ternary eutectic point L to the binary eutectic point P), and an interval of pure solution (from the binary eutectic point P to the melting point Q).

§ 44. We shall now suppose that the two salts S_1 and S_2 do not form a double salt, but that the simple salt S_1 can form a crystalline hydrate, which can be in stable equilibrium with solutions and which we will denote by H_1. There are again four solid phases which can occur in the system, namely Ice, S_1, S_2 and H_1, but this case is simpler than that in which a double salt forms the fourth solid phase, since the existence of the hydrate H_1 will always be limited to the lower temperature ranges, whilst the anhydrous salt S_1 will be incapable of existing in stable equilibrium with ice and saturated solutions. The only solid phase triads which can possibly exist in invariant equilibrium with a liquid phase in this condensed system are therefore the following:

$S_1 + S_2 + H_1 +$ Solution . . . 1.
Ice $+ S_2 + H_1 +$ Solution . . . 2.

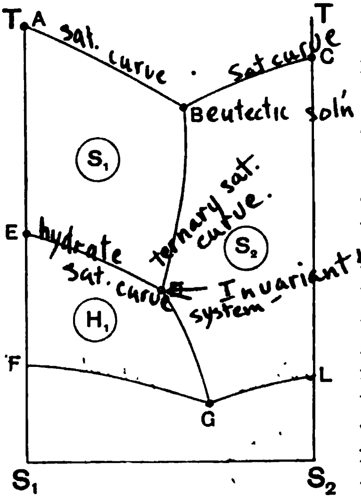


FIG. 53.

The conditions of equilibrium in the ternary system are represented for this case by Fig. 53. No compound can occur in the binary system S_1–S_2, and it is, therefore, of the simplest type, showing only the saturation curves AB and CB, of S_1 and S_2 respectively. The point B represents the composition of the eutectic solution which is in equilibrium with $S_1 + S_2$ in the anhydrous binary system, and the ternary saturation curve BD, of $S_1 + S_2$, must diverge from it in the direction of falling temperature. At a certain temperature the formation of the hydrate H_1 will become possible, and the curve BD will therefore be bounded on the side of low temperatures by the appearance of the hydrate as a third solid phase, and the formation of the system No. 1, which is in a state of invariant equilibrium. The conditions of equilibrium in this invariant system are represented by the system invariant point D of Fig. 53. If heat is added to, or withdrawn from, the invariant system, the phase reactions which will occur at constant temperature must be such as to maintain the constant composition of the liquid phase. Let us suppose that on withdrawing heat from the invariant solution D in contact with the three solid phases S_1, S_2, and H_1 a certain amount of the salt S_2 is deposited, then it is clear that if the solution is to remain unaltered in composition, both the weight of water and that of the salt S_1 in the liquid phase must be reduced proportionately. The weight of water in the liquid phase can only be reduced to the necessary value by the simultaneous separation of a definite weight of the solid hydrate H_1. This separation will, at the same time, effect a decrease in the weight of the third component S_1 contained by the liquid phase, but this decrease may be either too small or too great to leave the composition of the solution unchanged, and the third solid phase S_1 may, therefore, either separate or redissolve, according to the relative compositions of the liquid phase and the solid hydrate. Either of the following phase reactions may therefore occur on the withdrawal of heat from the invariant system:

$$\text{Solution } D \rightarrow H_1 + S_2 + S_1,$$

in which all three solid phases are formed at the expense of the liquid phase, or:

$$\text{Solution } D + S_1 \rightarrow H_1 + S_2,$$

in which only the two solid phases H_1 and S_2 are formed at the expense both of the liquid phase and the solid phase S_1.

The phase reactions in equilibrium at the system invariant point D may, therefore, be represented by either of the following notations:

$$H_1 + S_2 + S_1 \rightleftarrows \text{Solution } D \quad . \quad . \quad . \quad 3.$$

or

$$H_1 + S_2 \rightleftarrows \text{Solution } D + S_1 . \quad . \quad . \quad 4.$$

where the upper arrow indicates the phase reaction which occurs on the addition of heat to the invariant system, the lower arrow that which occurs on the withdrawal of heat from it. In the case represented by the notation No. 3, the system invariant point D is a eutectic point, since the phase reaction which occurs on the withdrawal of heat must eventually result in the total disappearance of the liquid phase at constant temperature. In the case represented by the notation No. 4, the phase reaction which occurs on the withdrawal of heat may result first in the disappearance of the solid phase S_1 and the formation, at lower temperatures, of the monovariant system $H_1 + S_2 +$ Solution ; in this case, the system invariant point D is not a lower temperature limit to the existence of the liquid phase—it is a transition point.

We see that, as in the binary system, so too in the ternary system, the polythermal type is dependent upon the relations which exist between the composition of the phases in equilibrium at the invariant point, when the salt hydrate forms one of those phases. We shall discuss in this paragraph only the case in which the system invariant point D is a transition point, when, therefore, the phase reactions in equilibrium at this point are given by the notation No. 4; this is the more usual case, and it is the one represented in Fig. 53. (We shall investigate the ternary system in which a salt hydrate appears as a solid phase more fully in Chapter V.) In this case, the monovariant system H_1–S_2–Solution is stable at temperatures below that of the transition point D. The corresponding polythermal saturation curve, DG, of $H_1 + S_2$, diverges therefore from the transition point D in the direction of falling temperatures, and it ends in the eutectic point G, which represents the solution in equilibrium, not only with $H_1 + S_2$, but also with the third solid phase ice (Invariant system No. 2). The phase reactions in equilibrium at this eutectic point are:

$$H_1 + S_2 + \text{Ice} \rightleftharpoons \text{Solution } G.$$

The three curves which diverge from it are the saturation curves GD, GF, and GL, of $H_1 + S_2$, $H_1 +$ Ice, and $S_2 +$ Ice respectively. The first terminates, as we have seen, in the transition point D, the two latter in the corresponding binary eutectic points F and L.

When heat is added to the system in equilibrium at the transition point, the following phase reaction occurs:

$$H_1 + S_2 \rightarrow \text{Solution } D + S_1,$$

and the two following monovariant systems can therefore exist at temperatures above the transition temperature:

$$S_2 + S_1 + \text{Solution},$$
$$H_1 + S_1 + \text{Solution}.$$

The curve DB, corresponding with the first of these, is the saturation curve of $S_1 + S_2$ which we have already mentioned, and it ends at the eutectic point B in the binary system S_1–S_2. The curve DE is the saturation curve of $H_1 + S_1$, and it ends in the binary system invariant point E, which represents a binary solution also in equilibrium with these two solid phases. We saw in the previous chapter that a binary system invariant point such as E, which represents a solution in equilibrium with $H_1 + S_1$ in the binary system W–S_1, may be either a transition point or a eutectic point, according to the relations which exist between the composition of the invariant solution and that of the hydrate. In most cases the binary invariant point E and the ternary invariant point D will be either both transition points or both eutectic points, although this is not necessarily the case; we shall assume that the binary invariant point E in Fig. 53, like the ternary invariant point D, is a transition point.

At the transition point E the following phases are in invariant equilibrium in the binary system W–S_1:

$$H_1 + S_1 + \text{Solution } E\,;$$

both the hydrated and the anhydrous salt exist in equilibrium with a binary liquid phase, and the point E is called the binary transition point of the hydrate.

At the transition point D, the following phases are in invariant equilibrium in the ternary system W–S_1–S_2:

$$H_1 + S_1 + S_2 + \text{Solution } D\,;$$

both the hydrated and the anhydrous salt are here in equilibrium with a ternary liquid phase, and the fourth phase, which is essential to the existence of the ternary invariant system, is the second solid salt S_2. The point D is called the ternary transition point of the hydrate; and the polythermal saturation curve ED, of $H_1 + S_1$, which ends in this point, can be considered as giving the lowering of the binary transition temperature due to the addition of increasing amounts of the third component S_2.

The various saturation surfaces are marked in Fig. 53 with the corresponding solid phases, and it can be seen that the ternary transition point D of the hydrate gives the lowest temperature at which anhydrous S_1 can exist as a solid phase in equilibrium with saturated ternary solutions. Below this point a line of constant temperature will intersect only the saturation surfaces of H_1 and S_2, and the only isothermal saturation curves which can occur in an isotherm below this temperature are those of H_1 and S_2. The only isothermal invariant point will therefore be that which represents a solution saturated with $H_1 + S_2$, and which corresponds with the point of intersection of the constant temperature line with the polythermal saturation curve *DG* of $H_1 + S_2$. The isothermal type is given, in this case, by Fig. 22 of § 31.

The temperature of the binary transition point *E* is the highest at which the hydrate can exist as a solid phase in equilibrium with ternary solutions, and a line of constant temperature above this point will intersect only the saturation surfaces of S_1 and S_2, and the polythermal saturation curve *DB* of $S_1 + S_2$. The isothermal types above this temperature will therefore be identical with those which we deduced for the simplest system in the higher temperature ranges.

Between the binary transition point *E* and the ternary transition point *D*, a line of constant temperature will intersect all three saturation surfaces. The isotherms between these temperatures must therefore show the isothermal saturation curves of H_1, S_1, and S_2 in order, and the isothermal invariant points which represent solutions saturated with $H_1 + S_1$ and $S_1 + S_2$, and which correspond with the points of intersection of the constant temperature line with the polythermal saturation curves *DE* and *DB*, of $H_1 + S_1$ and $S_1 + S_2$ respectively. The isothermal type within this temperature range will therefore be that discussed in § 32 and represented in Fig. 23.

If the second salt S_2 can also form a hydrate H_2, then the relations are somewhat more complicated, but they can readily be deduced by the methods which we have previously adopted. This case is depicted in Fig. 54, where the assumption is made that the second hydrate possesses, like the first, a transition point in the ternary system. This point is represented by *J* in the figure, and the ternary transition temperature of the hydrate H_2 is supposed to be higher than that of the hydrate H_1, which is given by the point *D*. As before, the ternary saturation curve *BJ*, of $S_1 + S_2$, diverges from the corresponding binary eutectic point B, and it is bounded on the side of low temperatures by the appearance of a hydrate as a third solid phase. This will be the hydrate H_2, since the latter has a higher transition temperature than has the hydrate H_1. The conditions of equilibrium are then represented by the system invariant point J, and since this point is a transition point the reactions in equilibrium are:

$$H_2 + S_1 \rightleftarrows \text{Solution } J + S_2.$$

Besides the saturation curve of $S_1 + S_2$, that of $H_2 + S_2$ must, therefore, diverge from the point J in the direction of rising temperature, and it reaches its maximum in the binary system invariant point K, at which the hydrate H_2 and the anhydrous salt S_2 are in equilibrium with a saturated solution in the binary system W–S_2; we may assume this point to be a transition point also.

The saturation curve JD, of $H_2 + S_1$, diverges from the point J in the direction of falling temperature, and it must be bounded on the side of low temperatures by the appearance of the hydrate H_1, as a third solid phase. At the system invariant point D the four phases:

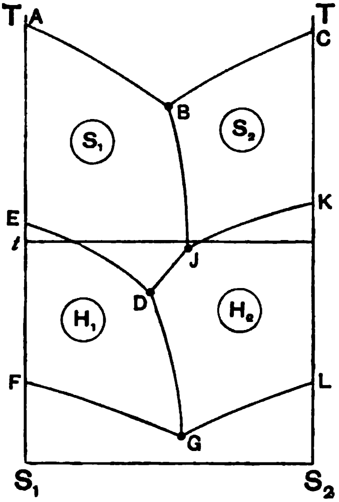


FIG. 54.

$$H_2 + S_1 + H_1 + \text{Solution } D$$

are in a state of invariant equilibrium. This point is the ternary transition point of the hydrate H_1, for this hydrate and the anhydrous salt S_1 are both in invariant equilibrium with a ternary solution, the third solid phase which partakes in this invariant equilibrium being the hydrate H_2. The phase reaction in equilibrium are therefore represented by the following notation:

$$H_1 + H_2 \rightleftarrows \text{Solution } D + S_1.$$

The saturation curves of $H_2 + S_1$ and $H_1 + S_1$ diverge from the point D in the direction of rising temperatures. The former ends in the ternary transition point J, as we have already seen, and the latter ends in the binary transition point E. The saturation curve of $H_1 + H_2$ diverges from the point D in the direction of falling temperature, and it ends in the ternary eutectic point G, where a liquid phase is in equilibrium with three solids $H_1 + H_2 +$ Ice. The reactions in equilibrium at this eutectic point are :

$$H_1 + H_2 + \text{Ice} \rightleftharpoons \text{Solution } G,$$

and the saturation curves of $H_1 +$ Ice, $H_2 +$ Ice and $H_1 + H_2$ all diverge from it in the direction of rising temperature ; the two former end in the corresponding binary eutectic points F and L, the latter in the ternary transition point D.

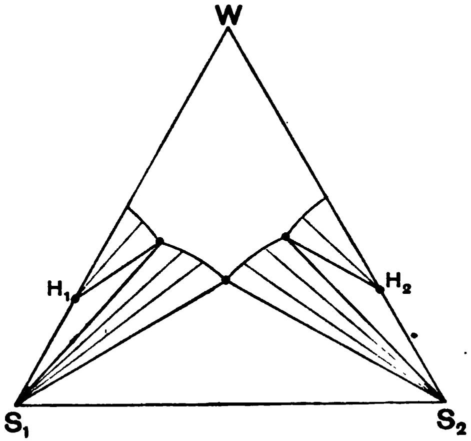


FIG. 55.

The isothermal types which may occur in this case depend upon the relative position of the various binary and ternary transition points. If the relations are those represented in Fig. 54, then the isotherm may contain at different temperatures one, two, or three isothermal invariant points. The constant temperature line t in Fig. 54, for example, is seen to cut four saturation surfaces and three polythermal saturation curves. The isotherm at this temperature (Fig. 55) contains the isothermal saturation curves of H_1, S_1, S_2, and H_2 in order, and three isothermal invariant points which represent solutions saturated with $H_1 + S_1$, $S_1 + S_2$, and $S_2 + H_2$. If the temperature of the binary transition point E lies below that of the ternary transition point J, and not above it as in the figure. this type cannot occur.

A discussion of the ternary system in which the ternary compound (the double salt hydrate) appears as solid phase will be given in a later chapter (Chapter V).

§ 45. Many condensed ternary systems composed of water and two salts have been investigated experimentally, and the results are to be found in the chemical literature. It is outside the scope of this book to give a complete bibliography of these investigations, and we shall therefore content ourselves with a brief discussion of a few of them.[1]

We have, hitherto, always used one of two different mathematical forms for expressing the composition of the liquid phase. In the first of these the concentrations of the three components were so chosen that their sum was constant and equal to 100:

$$W + S_1 + S_2 = 100,$$

where the letters W, S_1, and S_2 denote the concentrations of the corresponding components. The method of graphical representation to be used when the composition of the liquid phase is expressed in this way is the triangular method.

If the equilibrium conditions represented by points in the triangle refer to a constant temperature, then each solid phase which can occur at the considered temperature possesses its own saturation curve in the isotherm. If, on the other hand, the polythermal conditions of equilibrium are represented within the triangle, then points on the saturation curves represent solutions saturated with two solid phases and the temperature varies from point to point along the curves, its actual value at any point being unexpressed (§ 37).

In the second mathematical form which we have used the concentrations of the two salts S_1 and S_2 were so chosen that their sum was constant and equal to 100:

$$S_1 + S_2 = 100.$$

In this case the method of representation to be used is the rectangular method of Jänecke. We adopted this method in the preceding paragraphs to represent the polythermal relations in the ternary system, and for this purpose we measured along the vertical axis the temperature, and along the horizontal axis the composition of the salt mixture contained by saturated solutions (§ 38). The value of the temperature corresponding with any point on a saturation curve thus received graphical expression, but the water content of solutions remained unexpressed. It is clear that we could also represent the isothermal relations at any given temperature by Jänecke's method, for in order to do this it would only be necessary to measure the water content of solutions along the vertical axis instead of the temperature, which does not now vary. The resulting picture would give the complete isothermal conditions of equilibrium represented within a rectangle instead of the triangle which we have always used.

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[1] A large number of ternary systems are described in Schreinemakers' book, "Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," Roozeboom, Vol. III.

There is a third method which the reader will often meet in the literature, and which refers the concentration of the components in the liquid phase to a constant water content of 100:

$$W = 100.$$

The composition of the liquid phase is then written in the form

$$100 W, xS_1, yS_2,$$

and the graphical representation of the isothermal conditions of equilibrium is very simple. Two rectangular axes are chosen and the weight of S_1 contained in 100 parts of water is measured parallel to one axis, the weight of S_2 contained in 100 parts of water being measured parallel to the other axis. This method of representation was used by van't Hoff in his classical researches on the oceanic salt deposits. We have already emphasised the fact that the isothermal or polythermal type in any particular case is not dependent upon the method of graphical representation employed; the shapes of the various curves and fields are alone affected by a change in the method of representation.

We shall now illustrate some of the isothermal types which have been deduced in the theoretical treatment of the ternary system. The isotherm in the system H_2O–$(NH_4)_2SO_4$–NH_4Cl at 30°[1] is represented diagrammatically in Fig. 56 by means of a triangle, in Fig. 57 by means of a rectangle, and in Fig. 58 by means of rectangular axes. The system at 30° belongs to the simplest type, neither double salt nor salt hydrate occurring

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[1] Schreinemakers, *Zeitsch. physikal Chem.*, 1909, 69, 557.

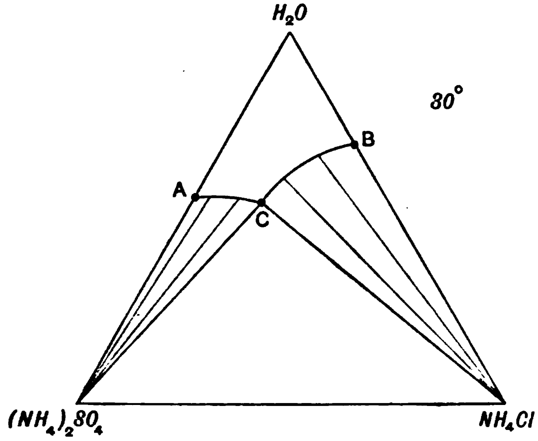

FIG. 56.

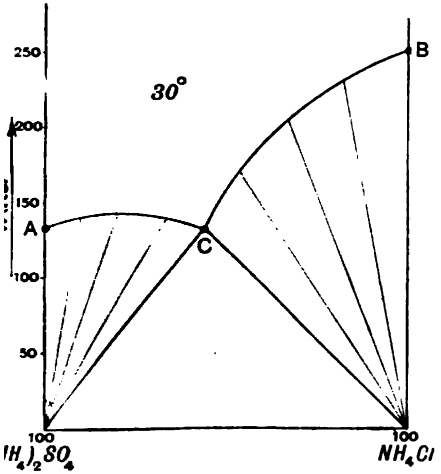

FIG. 57.

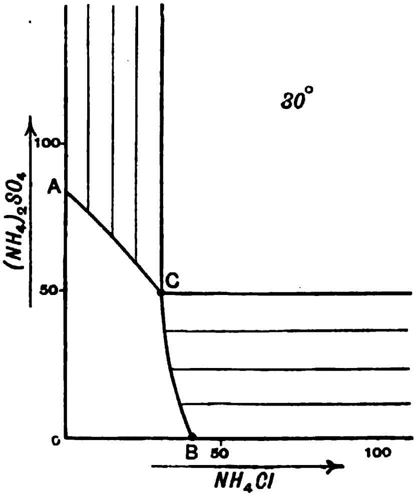

FIG. 58.

at this temperature. The point *A* in each of the three figures gives the composition of the saturated solution of ammonium sulphate at 30° in the binary system H_2O–$(NH_4)_2SO_4$. The actual composition of this solution, expressed in the three necessary forms, is approximately:

NH_4Cl.	$(NH_4)_2SO_4$.	H_2O.	
0	44	56,	where $W + S_1 + S_2 = 100$.
0	100	127,	where $S_1 + S_2 = 100$.
0	78·6	100,	where $W = 100$.

The composition of the saturated solution in the binary system H_2O–NH_4Cl is represented by the point *B*, and it is

NH_4Cl.	$(NH_4)_2SO_4$.	H_2O.	
29·5	0	71·5,	where $W + S_1 + S_2 = 100$.
100	0	242,	where $S_1 + S_2 = 100$.
41·3	0	100,	where $W = 100$.

The point *C* represents the isothermal invariant solution saturated with both ammonium sulphate and ammonium chloride. Its composition is:

NH_4Cl.	$(NH_4)_2SO_4$.	H_2O.	
17·6	25·7	56·7,	where $W + S_1 + S_2 = 100$.
40·6	59·4	131,	where $S_1 + S_2 = 100$.
31	45·3	100,	where $W = 100$.

All three figures show two saturation curves, that of ammonium sulphate and that of ammonium chloride. Points on one or other of these saturation curves may be obtained by reference to the original. Fig. 56 differs from the other two figures in that it treats all three components symmetrically, whilst Figs. 57 and 58 are peculiar in respect to their representation of the water component. Thus, points in Fig. 57 (Jänecke's representation) give the weight of water in a solution which contains 100 parts of the mixed salts. The point which represents pure water in this figure is, therefore, removed to an infinite distance along the vertical axis, since pure water represents the limiting case of solutions which are formed by a very large weight of water to 100 parts of the mixed salts. In this representation the area of unsaturated solutions is clearly of unbounded extent.

Points in Fig. 58 give the weight of each of the salts contained in solution by 100 parts of water. Pure water is therefore represented in this diagram by the origin of co-ordinates 0, since, at this point, the weight of both salts contained by 100 parts of water is zero. Pure ammonium sulphate is represented, however, by a point infinitely far removed along the ammonium sulphate axis, since it represents the limiting case of complexes which are formed by a very large weight of ammonium sulphate to 100 parts of water. Pure ammonium chloride is similarly represented, in this figure, by a point infinitely far removed along the ammonium chloride axis. The conjugation lines which start from points on the saturation curve of ammonium sulphate, end in the point representing pure ammonium sulphate, and since this point is infinitely far removed along the corresponding axis, they must run parallel to this axis. Similarly, the conjugation lines which start from points on the saturation curve of ammonium chloride must run parallel to the ammonium chloride axis. The complex areas, and the area of unsaturated solutions, are all of unbounded extent in this method of representation.

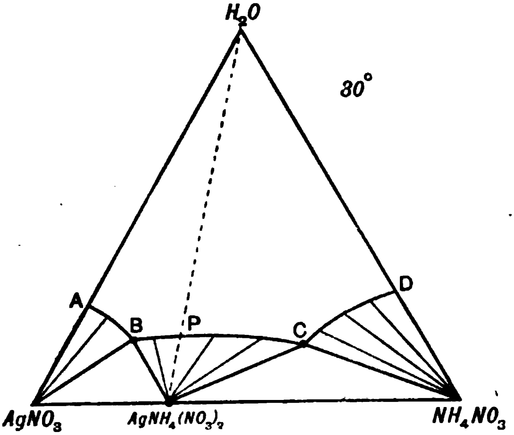

Fig. 59.

In the examples which follow we shall use the triangular method only for the representation of the isotherm. The conditions of equilibrium at 30° in the systems

$$H_2O–AgNO_3–NH_4NO_3 \text{ and } H_2O–AgNO_3–KNO_3{}^1$$

are represented in Figs. 59 and 60 respectively. In the first of these a double salt of the composition $AgNH_4(NO_3)_2$ occurs as a solid phase, and its composition is represented by a point on that side of the triangle which joins the vertices representing

[1] Schreinemakers, *Chem. Weekblad*, 1910, 7, 259, and *Zeitsch. physikal Chem.*, 909, 65, 576.

the two simple salts. There are three saturation curves in the isotherm: *AB* that of $AgNO_3$, *BC* that of $AgNH_4(NO_3)_2$, and *CD* that of NH_4NO_3. The points *B* and *C* give the compositions of the invariant solutions saturated at 30° with $AgNO_3 + AgNH_4(NO_3)_2$, and with $NH_4NO_3 + AgNH_4(NO_3)_2$ respectively. The line joining the point which represents the double salt to the water vertex cuts the saturation curve *BC* of the double salt, and this salt dissolves, therefore, in water, without decomposition at this temperature. The point of intersection *P* gives the composition of the saturated solution in the binary system H_2O–$AgNH_4(NO_3)_2$ at 30°, and the isotherm is divided by the dotted line H_2O – $AgNH_4(NO_3)_2$ into two parts which give the conditions of isothermal equilibrium in the simple ternary systems H_2O–$AgNO_3$–$AgNH_4(NO_3)_2$, and H_2O–NH_4NO_3–$AgNH_4(NO_3)_2$.

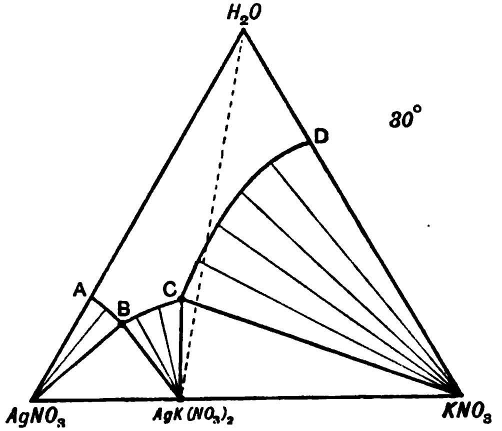

FIG. 60.

In the system H_2O–$AgNO_3$–KNO_3 (Fig. 60), a similar double salt, $AgK(NO_3)_2$, occurs as a solid phase at 30°. This isotherm differs, however, from the previous one in the fact that the line which joins the point representing the double salt to the water vertex does not intersect the saturation curve of the double salt. It intersects, instead, the saturation curve of potassium nitrate, and the double salt is therefore decomposed by water with the separation of solid potassium nitrate. The saturation curve *BC* of the double salt lies wholly within the triangle H_2O–$AgNO_3$–$AgK(NO_3)_2$, and the solid double salt can, therefore, only exist in stable contact with solutions which contain more silver nitrate in proportion to potassium nitrate than is contained by the double salt itself.

The two types illustrated by Figs. 59 and 60 have been discussed theoretically in §§ 27 and 30.

We mentioned in § 28 that more than one double salt may be capable of existing as a solid phase in the system at a given temperature. An example of this is found in the system H_2O-NH_4NO_3-$(NH_4)_2SO_4$; the isotherm at 30° is shown in Fig. 61.[1] This isotherm shows, besides the saturation curves *AB* and *ED*, of the simple salts $(NH_4)_2SO_4$ and NH_4NO_3, the saturation curves *BC* and *CD* of the two double salts

$$(NH_4)_2SO_4.(NH_4NO_3)_2 \text{ and } (NH_4)_2SO_4.(NH_4NO_3)_3.$$

If solid ammonium nitrate is added to the invariant solution *B* in contact with solid ammonium sulphate, the composition of the solution will not at first alter. The two simple salts will not, however, remain unchanged on the bottom of the containing vessel, but they will unite to form the double salt $(NH_4)_2SO_4.(NH_4NO_3)_2$, and the continued addition of ammonium nitrate will ultimately result in the conversion of the whole of the ammonium sulphate, present as a solid, into this double salt. The composition of the liquid will then change, and its successive values, as it becomes richer in ammonium nitrate, will be represented by points on the saturation curve *BC*. When the composition of the solution in contact with the double salt $(NH_4)_2SO_4.(NH_4NO_3)_2$ has reached the value represented by *C*, the addition of more ammonium nitrate will again be, at first, without effect upon the composition of the solution, and again ammonium nitrate will not remain unchanged as a second solid phase. It will

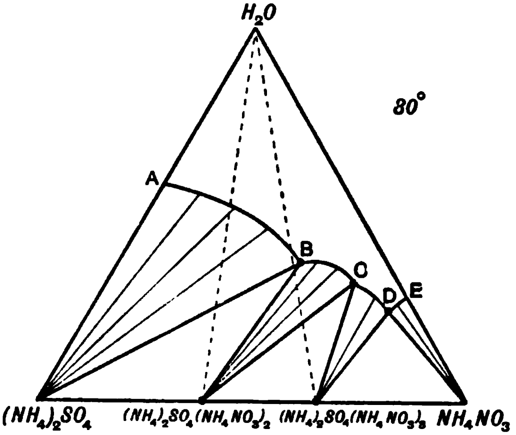

Fig. 61.

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[1] Schreinemakers, *Chem. Weekblad*, 1909, 6, 51.

unite with the first double salt to form the second double salt $(NH_4)_2SO_4.(NH_4NO_3)_3$, which is richer than the first in ammonium nitrate. The first double salt will eventually be consumed by this reaction, and solutions will then be obtained which are in equilibrium with the second double salt only, and which are represented by points on the curve *CD*. When the composition of the solution has finally reached that represented by the point *D*, ammonium nitrate will remain unchanged as a second solid phase in equilibrium with the double salt $(NH_4)_2SO_4.(NH_4NO_3)_3$ and the invariant solution *D*.

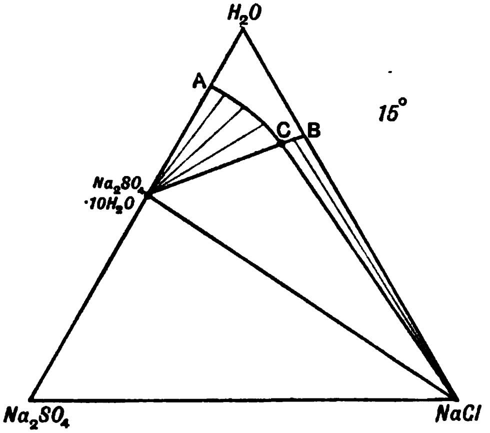

FIG. 62.

The system H_2O–$NaCl$–Na_2SO_4[1] is represented at 15° and 25° in Figs. 62 and 63 respectively. The stable solid phase in equilibrium with solutions in the binary system H_2O–Na_2SO_4 at both these temperatures is the decahydrate $Na_2SO_4.10H_2O$ (*cf.* Fig. 10). This hydrate is represented by a point on the side of the triangle in Figs. 62 and 63, and the binary saturated solution, represented by *A* in both figures, is in equilibrium

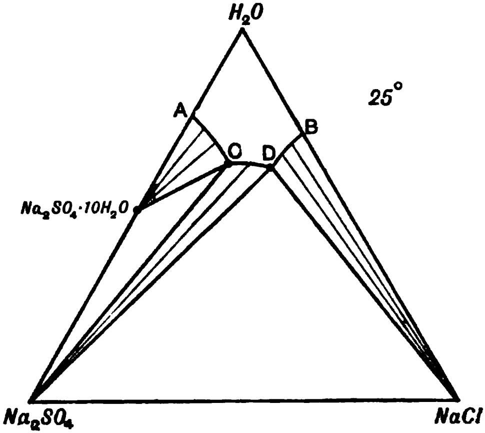

FIG. 63.

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[1] Seidell, *Amer. Chem. J.*, 1902, **27**, 52; Schreinemakers, *Zeitsch. physikal Chem.*, 1909, **67**, 553.

with it. In the ternary system at 15° (Fig. 62) the saturation curve *AC* of the hydrate $Na_2SO_4.10H_2O$ diverges from the point *A*, and ends in the invariant point *C*, which represents a solution saturated not only with $Na_2SO_4.10H_2O$, but also with sodium chloride.

In the isotherm at 25° (Fig. 63), the saturation curve *AC* of the decahydrate, $Na_2SO_4.10H_2O$, also diverges from the point *A*, but, when the concentration of sodium chloride in the solution has reached the value represented by the point *C*, dehydration of the hydrate occurs, and this point represents, therefore, the invariant solution in equilibrium with both hydrated and anhydrous sodium sulphate. The addition of sodium chloride to the solution *C*, in contact with sodium sulphate decahydrate, does not alter the composition of the solution until the hydrate has been completely dehydrated. The composition will then again alter and its successive values, as more sodium chloride is added, will be represented by points on the saturation curve *CD* of anhydrous sodium sulphate. At the composition represented by the point *D* the solution becomes saturated with sodium chloride, and the invariant solution *D* is, therefore, in equilibrium with the two solid phases Na_2SO_4 + NaCl. The two isothermal types illustrated by Figs. 62 and 63 have been discussed in §§ 31 and 32.

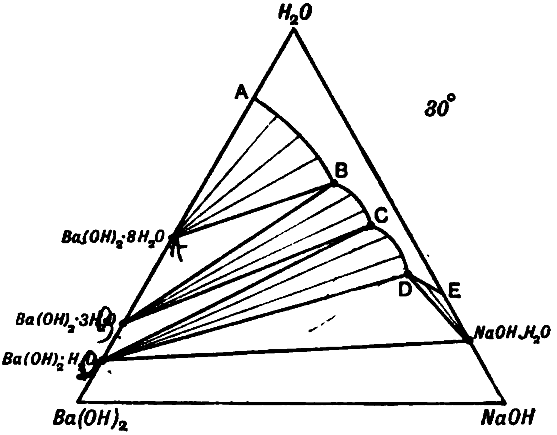

FIG. 64.

An example in which progressive dehydration of a hydrate occurs is afforded by the system H_2O–$Ba(OH)_2$–$NaOH$, which is represented, at 30°, in Fig. 64.[1] The stable solid phase at this temperature, in the binary system H_2O–$Ba(OH)_2$, is the octahydrate $Ba(OH)_2.8H_2O$, and the point *A* gives the composition of the binary solution saturated with this hydrate at 30°. The curve *AB* is the ternary saturation curve of $Ba(OH)_2.8H_2O$. When the concentration of sodium hydrate has reached a certain value, given by the point *B*, partial dehydration of the octahydrate occurs, and the trihydrate $Ba(OH)_2.3H_2O$ is formed. The point *B* represents the isothermal invariant solution which is in equilibrium with the two solid phases $Ba(OH)_2.8H_2O + Ba(OH)_2.3H_2O$, and the curve *BC* is the saturation curve of $Ba(OH)_2.3H_2O$. At a higher concentration of sodium hydrate, given by the point *C*, this trihydrate suffers partial dehydration in its turn, and the monohydrate $Ba(OH)_2.H_2O$ is formed. The point *C* represents the isothermal invariant solution which is in equilibrium with the two solid phases $Ba(OH)_2.3H_2O + Ba(OH)_2.H_2O$, and the curve *CD* is the saturation curve of the monohydrate. This hydrate is not further dehydrated at 30°, and at the composition represented by the invariant point *D* the solution becomes saturated with the hydrate $NaOH.H_2O$, which is the stable solid phase in the binary system H_2O–$NaOH$ at 30°; the point *E* gives the composition of the binary solution saturated with it at this temperature, and the curve *ED* is its saturation curve in the ternary system.

We shall now give a few examples of ternary systems in which the polythermal conditions of equilibrium will be represented by Jänecke's method. Although many ternary systems have been investigated over considerable temperature ranges, a complete and systematic investigation is, unfortunately, rare. It is generally necessary to collect the results from various sources, and to reduce them to the same mathematical form in order to obtain a graphical representation of the system, which, even then, must often remain incomplete.

The system H_2O–Na_2SO_4–$NaCl$ is represented diagrammatically in Fig. 65 as an illustration of the ternary system in which, besides the components, only simple hydrated salts can occur as solid phases, a case which we discussed in type in § 44.

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[1] Schreinemakers, *Zeitsch physikal Chem.*, 1909, 68, 83.

The point *A* (– 1·2°) in this figure is the eutectic point in the binary system H_2O–Na_2SO_4, and the point *B* (– 21·4°) is the eutectic point in the binary system H_2O–NaCl. The solid phases in equilibrium with these binary eutectic solutions are ice and the two hydrates $Na_2SO_4.10H_2O$ and $NaCl.2H_2O$ respectively (*cf.* Figs. 10 and 9). The points *A* and *B* form the starting points of the ternary saturation curves *AC* and *BC*, of Ice + $Na_2SO_4.10H_2O$ and Ice + $NaCl.2H_2O$ respectively, and these two curves intersect in the ternary eutectic point *C*. This point represents the ternary invariant solution which is in equilibrium with the three solid phases

$$\text{Ice} + Na_2SO_4.10H_2O + NaCl.2H_2O,$$

and the corresponding temperature is only slightly lower than that of the binary eutectic point *B*. The third curve *CD*, which diverges from the ternary eutectic point in the direction of rising temperature, is the saturation curve of the two hydrates $Na_2SO_4.10H_2O$ + $NaCl.2H_2O$. The first hydrate to suffer dehydration with rising temperature is the dihydrate of sodium chloride, and the saturation curve *CD* ends in the point *D* where anhydrous sodium chloride appears as a third solid phase. This point is the ternary transition point of the hydrate $NaCl.2H_2O$, and it represents the invariant solution which is in equilibrium with the three following solid phases :

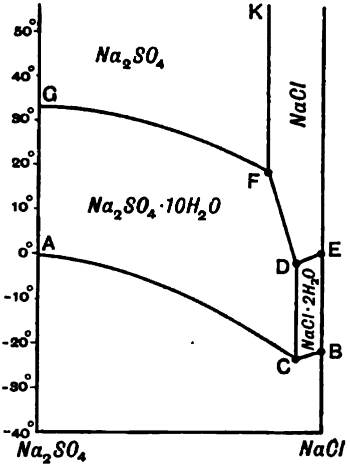

FIG. 65.

$$Na_2SO_4.10H_2O + NaCl.2H_2O + NaCl\,;$$

the corresponding transition temperature has not been determined. The two saturation curves *DE* and *DF*, of $NaCl.2H_2O$ + NaCl and of $Na_2SO_4.10H_2O$ + NaCl respectively, diverge from the transition point *D* in the direction of rising temperature. The former ends in the binary transition point *E* (+ 0.15°), at which both hydrated and anhydrous sodium chloride are in equilibrium with an invariant solution in the binary system H_2O–NaCl (*cf.* Fig. 9).

At a higher temperature the decahydrate of sodium sulphate also suffers dehydration, and the saturation curve *DF*, of $Na_2SO_4.10H_2O + NaCl$, ends in the invariant point *F* where anhydrous sodium sulphate appears as a third solid phase. The point *F* (17.9°) is, therefore, the ternary transition point of the hydrate $Na_2SO_4.10H_2O$, and it represents the invariant solution which is in equilibrium with the three following solid phases :

$$Na_2SO_4.10H_2O + Na_2SO_4 + NaCl.$$

The two saturation curves *FG* and *FK*, of $Na_2SO_4.10H_2O$ + Na_2SO_4 and of Na_2SO_4 + NaCl respectively, diverge from the transition point *F* in the direction of rising temperature. The former ends at the corresponding transition point *G* (32.5°) in the binary system H_2O–Na_2SO_4 (*cf.* Fig. 10), whilst the upper temperature limit of the latter is unknown. This curve must, however, extend continuously to the binary eutectic point in the anhydrous system Na_2SO_4–NaCl if the salts are not decomposed by water at this high temperature, if the liquid phase does not separate into two layers, and if the critical temperature of the mixture is not attained.

We can see from Fig. 65 that, between the temperatures 32·5° and 17·9°, of the binary transition point *G* and the ternary transition point *F*, a constant temperature line will cut the saturation surfaces of $Na_2SO_4.10H_2O$, Na_2SO_4, and NaCl in order. The isotherm in this system at 25° has already been given (Fig. 63), and, in agreement with this, it shows the isothermal saturation curves of $Na_2SO_4.10H_2O$, Na_2SO_4, and NaCl. At a temperature below that of the point *F* (17·9°), the constant temperature line cuts only the saturation surfaces of $Na_2SO_4.10H_2O$ and NaCl. The isotherm below this temperature will show, therefore, only the saturation curves of $Na_2SO_4.10H_2O$ and NaCl, as we have already seen to be the case at 15° (Fig. 62).

The system H_2O–$AgNO_3$–NH_4NO_3[1] offers an example of a ternary system characterised by the appearance of a double salt the existence interval of which extends over the whole temperature range within which saturated solutions are possible (§ 41). This system, which is represented diagrammatically in Fig. 66, is one of the very few systems, composed of two salts and water, in which the polythermal saturation curves have been shown to extend continuously to the corresponding binary eutectic points in the anhydrous salt system. The double salt $AgNH_4(NO_3)_2$ appears as a solid phase in the binary system $AgNO_3$–NH_4NO_3, and *CD* is its binary saturation curve. This curve passes through a temperature maximum *E* (109·6°), which gives the melting point of the pure double salt, whilst the points *A* (209)° and *B* (167·8°) give the melting temperatures of the pure simple salts, silver nitrate and ammonium nitrate respectively.

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[1] Schreinemakers, *Chem. Weekblad*, 1910, 7, 259.

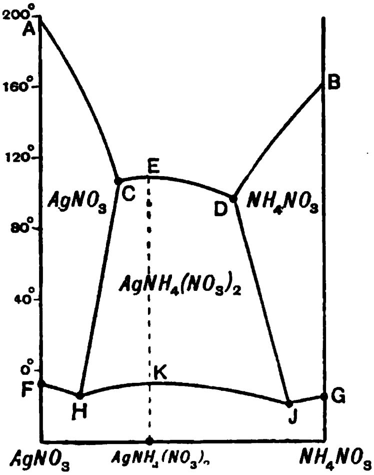

FIG. 66.

The point *C* (109·5°) is the binary eutectic point representing the composition of the anhydrous melt which is in equilibrium with the two solid phases

$$AgNO_3 + AgNH_4(NO_3)_2.$$

The ternary saturation curve *CH* diverges from this point in the direction of falling temperature, and points on it represent ternary solutions in equilibrium with these same two solid phases. This saturation curve ends in the ternary eutectic point *H* (− 14·9°), which represents the solution in equilibrium, not only with these two salts, but also with the third solid phase ice. In the same way, the point *D* (101·5°) represents the binary eutectic solution in equilibrium with the two solid phases $AgNH_4(NO_3)_2 + NH_4NO_3$, the curve *DJ* is the ternary saturation curve of these two solids, and the point *J* (− 18·7°) represents the ternary eutectic solution in equilibrium with the three solid phases $AgNH_4(NO_3)_2 + NH_4NO_3 +$ Ice.

The two ternary eutectic points *H* and *J* are joined by the ternary saturation curve *HJ* of $AgNH_4(NO_3)_2 +$ Ice. This curve reaches a maximum in the point *K* (− 14·8°), which represents a solution the composition of which can be expressed in terms of water and the double salt alone, and which is in equilibrium with both ice and the double salt. The system H_2O–$AgNH_4(NO_3)_2$ behaves, in fact, as a true binary system of the simplest type, and the point *K* is the eutectic point in this binary system. The ternary system H_2O–$AgNO_3$–NH_4NO_3 can be considered, at all temperatures, as built up from the two simpler systems H_2O–$AgNO_3$–$AgNH_4(NO_3)_2$ and H_2O–NH_4NO_3–$AgNH_4(NO_3)_2$. The isotherm at 30° has already been discussed (Fig. 59).

We shall give, finally, a few examples of the ternary system which is characterised by the occurrence of a double salt with a transition point. In the theoretical discussion of this case (§§ 39 and 40), we assumed that the double salt was anhydrous, and we saw that at the transition temperature the double salt and the two simple salts were all in equilibrium with an invariant liquid; on altering the temperature in one direction, decomposition of the double salt into the two simple salts occurred, and on altering it in the opposite direction, formation of the double salt from the two simple salts. In the examples which we give below the double salt is hydrated, but similar theoretical considerations apply; the double salt may break down, at temperatures above or below the transition point, into two simple anhydrous salts, into two simple salt hydrates, or into one simple salt hydrate and an anhydrous salt. Since the simple salt hydrate must, at some temperature, suffer dehydration, the examples given will be found to combine the types shown in Figs. 44 and 45 with those shown in Figs. 53 and 54.

The systems H_2O–Na_2SO_4–$FeSO_4$, H_2O–Na_2SO_4–$CoSO_4$, H_2O–Na_2SO_4–$NiSO_4$, and H_2O–Na_2SO_4–$ZnSO_4$[1] can all be represented diagrammatically by Fig. 67, where the heavy metal is denoted by *R*. In each of these systems a hydrated double salt occurs of the general formula $Na_2SO_4.RSO_4.4H_2O$, and this double salt possesses, in each case, a transition point which marks a lower stability limit to its existence as a solid in the system. In order to take a concrete example, we will suppose that the letter *R* in Fig. 67 denotes the metal zinc.

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[1] Koppel, *Zeitsch. physikal. Chem.*, 1903, **42**, 1; 1905, **52**, 408.

The transition point *A* corresponds, in this case, with a temperature of 8·7°, and it represents the invariant solution in equilibrium with the hydrated double salt and the two hydrated simple salts :

$$Na_2SO_4.ZnSO_4.4H_2O + Na_2SO_4.10H_2O + ZnSO_4.7H_2O.$$

At temperatures below that of the point *A* the double salt cannot exist in equilibrium with solutions, and the only saturation curve (*AB*) which diverges from the transition point in the direction of falling temperature is that of the two hydrated simple salts :

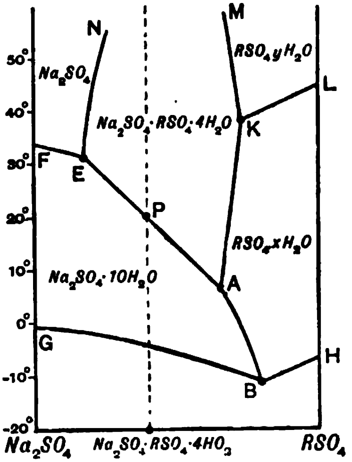

FIG. 67.

$$Na_2SO_4.10H_2O + ZnSO_4.7H_2O.$$

This saturation curve ends in the ternary eutectic point *B*, where ice appears as a third solid phase. At temperatures above that of the transition point, the two simple salt hydrates cannot exist together in equilibrium with solutions, and the two curves *AE* and *AK* which diverge from the point *A* in the direction of rising temperature are, therefore, the saturation curves of

$$Na_2SO_4.10H_2O + Na_2SO_4.ZnSO_4.4H_2O$$

and of $ZnSO_4.7H_2O + Na_2SO_4.ZnSO_4.4H_2O$

respectively. The saturation curve *AE* terminates on the side of high temperatures in the invariant point *E* (31·5°), where anhydrous sodium sulphate appears as a third solid phase. This point is the ternary transition point of sodium sulphate decahydrate, and the invariant solution which it represents is in equilibrium with the three solid phases :

$$Na_2SO_4.10H_2O + Na_2SO_4 + Na_2SO_4.ZnSO_4.4H_2O.$$

The two saturation curves *EF* and *EN*, which rise from the transition point *E*, represent solutions saturated with

$$Na_2SO_4.10H_2O + Na_2SO_4$$

and $Na_2SO_4 + Na_2SO_4.ZnSO_4.4H_2O$

respectively. The former ends in the binary transition point *F* (32·5°) of the decahydrate.

The saturation curve *AK* terminates similarly in the ternary transition point *K* (37·4°) of zinc sulphate heptahydrate, and this point represents the invariant solution in equilibrium with the three solid phases:

$$ZnSO_4.7H_2O + ZnSO_4.6H_2O + Na_2SO_4.ZnSO_4.4H_2O.$$

Complete dehydration of the hydrate $ZnSO_4.7H_2O$ does not occur at the transition point *K*, the hexahydrate $ZnSO_4.6H_2O$ appearing as the new solid phase.

The two saturation curves *KL* and *KM* represent solutions saturated with

$$ZnSO_4.7H_2O + ZnSO_4.6H_2O$$

and

$$ZnSO_4.6H_2O + NaSO_4.ZnSO_4.4H_2O$$

respectively. The former ends at the transition point *L* (39°), of the heptahydrate, in the binary system H_2O–$ZnSO_4$.

Every point on the dotted line in Fig. 67 represents a solution containing the simple salts in the same proportion as does the double salt. The lowest temperature at which the solid double salt can exist in the system is that of the transition point *A* (8·7°), but between this temperature and that of the point P ~~*F*~~ (21°) the dotted line traverses the saturation surface of the decahydrate $Na_2SO_4.10H_2O$, and not that of the double salt. This temperature range (8·7° to 21°) forms, therefore, the transition interval of the double salt, and within this range the latter is decomposed by water with the formation of the solid hydrate $Na_2SO_4.10H_2O$.

In the system H_2O–Na_2SO_4–$(NH_4)_2SO_4$[1] the hydrated double salt $NaNH_4SO_4.2H_2O$ occurs as a solid phase, and it possesses a transition point which, unlike the examples we have just discussed, forms an upper limit to its existence. The polythermal relations in this system are represented diagrammatically in Fig. 68, where the point *A* is the transition point of the double salt. The corresponding transition temperature is 59° and, since both the simple salts sodium sulphate and ammonium sulphate can only exist at this temperature in the anhydrous state, the following are the three solid phases which are in equilibrium with the invariant solution *A* :

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[1] Matignon and Meyer, *Compt. rend.*, 1917, **165**, 787; 1918, **166**, 155.

$$Na_2SO_4 + (NH_4)_2SO_4 + NaNH_4SO_4.2H_2O.$$

At temperatures above the transition temperature the double salt cannot exist in equilibrium with solutions and the curve *AK*, which diverges from the point *A* in the direction of rising temperature, is, therefore, the saturation curve of the two anhydrous salts :

$$Na_2SO_4 + (NH_4)_2SO_4.$$

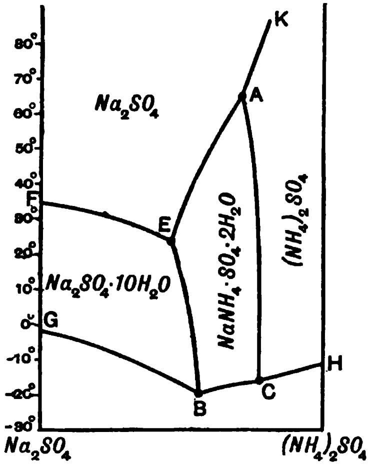

FIG. 68.

The curves *AC* and *AE*, which diverge from the point *A* in the direction of falling temperature, are the saturation curves of

$$(NH_4)_2SO_4 + NaNH_4SO_4.2H_2O$$

and of

$$Na_2SO_4 + NaNH_4SO_4.2H_2O$$

respectively. The former extends continuously to the ternary eutectic point *C* (– 21°) where ice appears as a third solid phase. The latter terminates, however, at a point *E* (26°), where the formation of sodium sulphate decahydrate occurs. The point *E* is the ternary transition point of this hydrate, and the invariant solution represented by it is in equilibrium with the following three solid phases :

$$Na_2SO_4 + Na_2SO_4.10H_2O + NaNH_4SO_4.2H_2O.$$

Below the temperature of the transition point *E* the anhydrous salt, Na_2SO_4, cannot exist as a solid phase, and the curve *EB*, which diverges from this point in the direction of falling temperature, is, therefore, the saturation curve of

$$Na_2SO_4.10H_2O + NaNH_4SO_4.2H_2O.$$

This curve ends in a second ternary eutectic point *B* (– 21°), where ice appears as a third solid phase. The curve *EF* is the saturation curve of :

$$Na_2SO_4 + Na_2SO_4.10H_2O,$$

and it ends at the corresponding transition point *F* (32·5°), of the decahydrate, in the binary system H_2O–Na_2SO_4.

It is clear that, between the temperature of the ternary transition point *E* (26°) and that of the binary transition point *F* (32·5°), an isotherm will show four saturation curves, namely, those of $Na_2SO_4.10H_2O$, Na_2SO_4, $NaNH_4SO_4.2H_2O$, and $(NH_4)_2SO_4$, in order.

§ 46. We saw in the previous chapter that the system formed by water and a simple salt offers, in the general case, an example of a binary system. We have seen further, that the system formed by water and a double salt is also a binary system, if the double salt is not decomposed by water into its constituent simple salts; but, if such a decomposition does occur, the compositions of phases can no longer be expressed in terms of water and the double salt alone, and the system becomes ternary.

It sometimes happens that a simple salt is decomposed by water according to the following scheme:

$$AB + H_2O \rightarrow HA + BOH,$$

where AB denotes a salt, HA and BOH the corresponding acid and base. When the salt AB is hydrolysed by water in this way, the system H_2O–AB may no longer be a binary system, since the acid or the base may separate in the solid phase, the composition of which will then no longer be capable of expression in terms of the salt and water alone. Such a system would, at first sight, appear to be a quaternary system of the four components AB, AH, BOH, and H_2O. These four components are, however, not all independent components, and the system is in reality a ternary system. Let us suppose, for example, that 100 gram molecular weights (which we will call 100 moles) of a certain solution contain x moles of the acid HA, and $100 - x$ moles of water. We can express the composition of this solution in molecular percentages by the form:

$$xHA, \overline{100 - x}H_2O,$$

or, since the equation

$$1 \text{ mole } HA = 1 \text{ mole } AB + 1 \text{ mole } H_2O - 1 \text{ mole } BOH$$

is *mathematically* true, we may express it in the form :

$$xAB, x\mathrm{H_2O}, -xBOH, (100-x)\mathrm{H_2O},$$

or

$$xAB, -xBOH, 100\mathrm{H_2O}.$$

If, therefore, we choose as three independent components AB, BOH, and H_2O, the compositions of all phases can be expressed in terms of these three, since the concentration of the acid HA can always be expressed, in virtue of the equation given above, in terms of AB, BOH, and H_2O.

It must be very clearly understood that the actual molecular condition of the liquid phase is quite immaterial to the present considerations. Whether we express the composition of the above solution in terms of the acid and water, or in terms of the salt, the base, and water, we do not imply that these substances actually exist as chemical individuals in the solution in these particular concentrations, or even that they exist at all. In the example which we have just given, the composition of a solution was expressed by the form :

$$xAB, -xBOH, 100\mathrm{H_2O},$$

a form which attributes a negative value to the concentration of the base. From a purely chemical point of view, this is devoid of meaning. The fact that the compositions of all phases of the system H_2O–AB–AH–BOH can be expressed *mathematically* in terms of three components establishes it as a ternary system, although an unlimited number of molecular species may exist. We may choose any three of the four substances AB, AH, BOH, H_2O as our independent components; whichever three we choose, however, the concentration of the fourth can only be expressed by assigning a negative value to the concentration of one of them. If, for example, we choose BOH, HA, and H_2O as independent components, then the concentration of the salt AB can be expressed in terms of these by means of the mathematical relation :

$$1 \text{ mole } AB = 1 \text{ mole } HA + 1 \text{ mole } BOH - 1 \text{ mole } \mathrm{H_2O},$$

which involves a negative value for the water concentration.

We may obviate the use of negative values by choosing as components water, and the corresponding acid and basic oxides. Let us consider, for example, a system formed from mixtures of water, sodium chromate, caustic soda and chromic acid. If we choose as components of this system water and the two oxides Na_2O and CrO_3, then the compositions of all possible mixtures can be expressed in terms of positive amounts of these components, since sodium chromate can be expressed in positive terms of Na_2O and CrO_3, caustic soda in positive terms of Na_2O and H_2O, and chromic acid in positive terms of CrO_3 and H_2O. This is the method generally used in dealing with systems of this type. Such systems, although of considerable practical interest, require no new theoretical consideration, and we shall confine ourselves, therefore, to the discussion of a few examples.

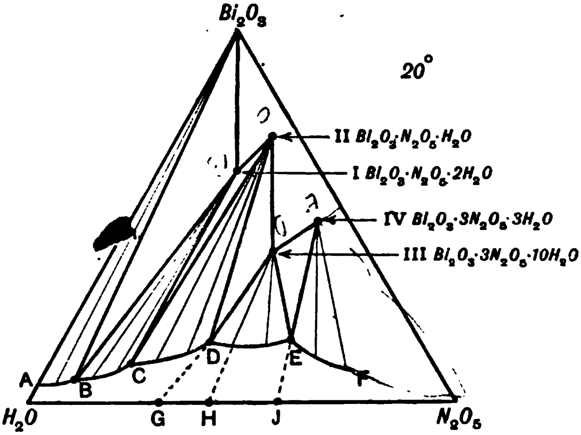
Bi_2O_3
20°
II $Bi_2O_3 \cdot N_2O_5 \cdot H_2O$
I $Bi_2O_3 \cdot N_2O_5 \cdot 2H_2O$
IV $Bi_2O_3 \cdot 3N_2O_5 \cdot 3H_2O$
III $Bi_2O_3 \cdot 3N_2O_5 \cdot 10H_2O$
A
B
C
D
E
F
H_2O
G
H
J
N_2O_5

FIG. 69.

§ 47. Bismuth nitrate, $Bi(NO_3)_3$, is a salt which is hydrolysed by water. The system H_2O-$Bi(NO_3)_3$ is, therefore, not a binary, but a ternary system. It has been investigated by Rutten and van Bemmelen[1] at various temperatures, and the isotherm at 20° is represented diagrammatically in Fig. 69 where water and the two oxides Bi_2O_3 and N_2O_5 are chosen as the components of the system.

The neutral nitrate of bismuth $Bi(NO_3)_3$ is then represented, in terms of these components, by the formula $Bi_2O_3.3N_2O_5$. The point *A* gives the concentration of bismuth oxide in its binary saturated solution. This concentration is exceedingly small, and it has been exaggerated in Fig. 69 for convenience in drawing; the point *A* lies, in reality, very close to the water corner. The curve *AB* is the ternary saturation curve of bismuth oxide; it is very short, and has not been experimentally realised. Solutions represented on the saturation curve *BC* are in equilibrium with a ternary compound the composition of which is expressed by the formula $Bi_2O_3.N_2O_5.2H_2O$. This compound is a hydrated basic salt, for it contains more bismuth oxide in proportion to the acid oxide than does the neutral salt. When the concentration of N_2O_5 (or of nitric acid) in the system has reached that represented by the point *C*, dehydration of this basic salt occurs, and the lower hydrate $Bi_2O_3.N_2O_5.H_2O$ is formed. The two basic salt hydrates are in equilibrium with the invariant solution *C*. The curve *CD* is the saturation curve of the basic salt monohydrate, and the curve *DE* is the saturation curve of the neutral salt hydrate $Bi_2O_3.3N_2O_5.10H_2O$, the composition of which is also represented by the formula $Bi(NO_3)_3.5H_2O$. The point representing this salt is marked as III in the figure, and the line which joins it to the water corner cuts the saturation curve of the basic, and not that of the neutral, salt. The latter is therefore decomposed by water with separation of the basic salt. The point *D* gives the composition of the invariant solution which is in equilibrium with both the monohydrated basic salt and the decahydrated neutral salt. Let the line joining III to *D* be continued to meet the side H_2O–N_2O_5 in the point *G*. This point *G* represents an aqueous solution of nitric acid of a certain concentration, and a point such as *H*, nearer than *G* to the N_2O_5 corner, represents an aqueous solution of nitric acid containing a greater percentage of the acid than does the solution *G*. Now the ternary solution formed by saturating the aqueous acid *H* with the hydrated neutral salt $Bi_2O_3.N_2O_5.10H_2O$ must be represented on the line joining III to *H*, and since this line cuts the saturation curve of the neutral salt, the resulting solution is in equilibrium with the latter. Thus the neutral salt, although decomposed by water, is stable in the presence of an aqueous solution of nitric acid containing more acid than the solution *G*.

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[1] *Zeitsch. anorg. Chem.*, 1902, **30**, 408.

On continuously increasing the concentration of nitric acid a point is reached where the salt $Bi_2O_3.N_2O_5.10H_2O$ is partially dehydrated with the formation of the lower hydrate $Bi_2O_3.3N_2O_5.3H_2O$. The curve *EF* is the saturation curve of this trihydrate, and the point *E* represents the composition of the invariant solution in equilibrium with both the tri- and the deca-hydrated neutral salt. The trihydrate is also decomposed by water with separation of the basic salt. It is clearly converted into the deca-hydrate by aqueous solutions of nitric acid the compositions of which are represented between the points *G* and *J*, whilst it is stable in presence of nitric acid more concentrated than that represented by the point *J*. The system has not been investigated at higher N_2O_5 concentrations than that given by the point *F*. It is possible that there exists a fifth invariant point, nearer to the N_2O_5 corner than the point *F*, where the trihydrate is further dehydrated to the anhydrous neutral salt.

Neutral mercuric sulphate ($HgSO_4$) and water also form a ternary system, since this salt is hydrolysed by water. The system H_2O–HgO–SO_3 has been investigated at 25° and at 50°;[1] it closely resembles, in type, the system which we have just discussed. The isotherm at 25° contains five saturation curves: that of HgO, those of the anhydrous basic salt $3HgO.SO_3$ and of the hydrated basic salt $3HgO.2SO_3.2H_2O$, and those of the neutral salt monohydrate $HgO.SO_3.H_2O$ and of the anhydrous neutral salt. In this case also, both the hydrated and the anhydrous neutral salts are decomposed by water with the separation of a basic salt.

It is clear that a study of the conditions of equilibrium in the system composed of water, a basic, and an acid oxide, must reveal all compounds of the two oxides which are capable of existing in the solid state in contact with a liquid phase. It will show not only the conditions under which the neutral salt is capable of existing, but it will also show what basic and acidic salts can exist, and the conditions under which they may be in equilibrium with solutions. A large number of previously unknown salts have been discovered in this way.

The systems H_2O–CrO_3–M_2O, where M_2O is the oxide of one of the alkali metals, lithium, sodium, potassium, rubidium, cæsium, or ammonium, have all been investigated at 30°.[2]

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[1] Hoitsema, *Zeitsch. physikal Chem.*, 1895, **17**, 651.

[2] Schreinemakers, *Zeitsch. physikal Chem.*, 1906, **55**, 71; *Chem. Weekblad*, 1906, **3**. 157; 1908, **5**, 811.

There exist no fewer than six compounds in the system H_2O–Na_2O–CrO_3 at this temperature, each with its corresponding isothermal saturation curve; they are anhydrous sodium chromate, $Na_2O.CrO_3$, and its tetrahydrate, $Na_2O.CrO_3.4H_2O$, the hydrated basic chromate, $2Na_2O.CrO_3.13H_2O$, and the three hydrated acid chromates, $Na_2O.2CrO_3.2H_2O$ (sodium di-chromate), $Na_2O.3CrO_3.H_2O$ (sodium trichromate), and $Na_2O.4CrO_3.4H_2O$ (sodium tetrachromate). All these dissolve in water without decomposition.

If the neutral salt is not decomposed by water, and we wish to investigate only the acid salts in a given system, we may choose as components water, the neutral salt, and the acid, or, if we wish to investigate only the basic salts, then we may choose water, the neutral salt, and the base, as components. The system the components of which are H_2O–Li_2SO_4–H_2SO_4[1] shows at 30°, for example, the saturation curve of the acid salt, $LiHSO_4$, and the system H_2O–$BaCl_2$–$Ba(OH)_2$,[2] at the same temperature, shows the saturation curve of the hydrated basic salt, $BaCl_2.Ba(OH)_2.H_2O$.

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[1] D'Ans, *Zeitsch. anorg. Chem.*, 1906, **49**, 356; 1909, **61**, 91.

[2] Schreinemakers, *Zeitsch. physikal Chem.*, 1909, **68**, 85.

CHAPTER III

CONDENSED QUATERNARY SYSTEMS

§ 48. **Systems** formed by water and three salts having a common ion are quaternary systems, provided that no one of the three salts is hydrolysed by water. The salts can be represented by *AD*, *BD*, and *CD*, where the common ion *D* may be either basic or acidic, and the composition of the liquid phase, which we assume to be the only phase of varying composition, can be expressed in terms of water, *AD*, *BD*, and *CD*. It follows from the phase theory that, when five phases are in equilibrium with each other in this condensed four component system at constant pressure, the equilibrium is invariant. Four solid phases can exist in stable contact with solution, only at a definite temperature, and the composition of the solution will then have a definite value. Three solid phases in equilibrium with solution constitute a monovariant quaternary system. At a given temperature within a certain range, there can exist one solution of definite composition, saturated with three salts. Such a solution is, therefore, an isothermal invariant solution. The quaternary system in which two solid phases are in equilibrium with solution possesses two degrees of freedom. At a fixed temperature one other condition must be fixed (let us say the concentration of the salt *AD* in the solution) before all the conditions of equilibrium become defined; when the concentration of *AD* has been fixed, then the concentrations of the other two salts *BD* and *CD* also become fixed, and to every concentration of the one salt there corresponds, within certain limits, definite concentrations of the other two salts at the temperature considered. We may say that the quaternary solution in equilibrium with two solid salts forms a monovariant system at *constant temperature*, and the compositions of such solutions must, therefore, be represented by points on an isothermal saturation curve. Quaternary systems composed of one solid phase in equilibrium with solution possess a still greater variability. Solutions saturated with one salt are represented by points on an isothermal saturation surface, since, at a given temperature, it is necessary to fix the concentrations of two of the salts in order completely to define the system.

We shall now consider how the conditions of equilibrium in the quaternary system *W–AD-BD–CD* can be represented graphically.

§ 49. We shall again express the concentration of each component in the liquid phase as a weight percentage of the whole solution. If we denote the three salts and water by the symbols S_1, S_2, S_3, and W, then the composition of the liquid phase will be expressed in the form :

$$xS_1,yS_2,zS_3,(100-\overline{x+y+z})W.$$

The composition of a quaternary solution involves, therefore, three independent concentration factors x, y, and z, and the relations which exist at a fixed temperature, between the concentrations of the salts in the various saturated solutions, can, therefore, only be represented graphically in space. The complete quaternary isotherm is a space figure.

We have seen that the use of a triangle to represent isothermal relations in the ternary system enables us to express graphically, not only the two independent concentration variables, but also the third dependent variable, which is related to the other two by the fact that the sum of the three equals 100. This was a result of the geometrical property of an equilateral triangle, that the sum of the distances of a point inside the triangle from the three sides, and in directions parallel to those sides, is constant and equal to the length of the side of the triangle.

We shall now show that it is possible to represent the composition of a quaternary mixture by a point inside a space figure in such a way as to express, not only the three independent concentration factors, x, y, and z, but also the dependent factor $100-\overline{x+y+z}$.

In Fig. 70, $WS_1S_2S_3$ is a regular tetrahedron, that is, a pyramid the base of which, S_1S_2,S_3, and each of the faces of which, WS_1S_2, WS_2S_3, WS_3S_1, is an equilateral triangle. The six edges of the tetrahedron (namely, S_1S_2, S_2S_3, S_3S_1, WS_1, WS_2, and WS_3) are, therefore, all equal in length. *P* is a point inside the tetrahedron, and through this point six lines are drawn parallel to the six edges of the tetrahedron. These six lines are *EF*, *AB*, *CD*, *LM*, *GH*, *JK*, parallel, respectively, to the six edges enumerated above, and they form the edges of four smaller tetrahedra having a common vertex in *P*. One

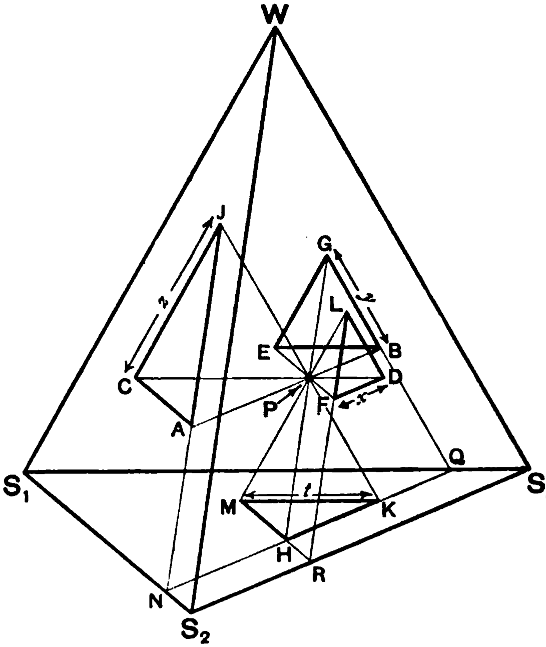

FIG. 70.

face of each of the smaller tetrahedra lies in a face of the large tetrahedron. Let the length of the edge of the tetrahedron *P–DFL* be called *x*, that of the tetrahedron *P–BEG*, *y*, that of the tetrahedron *P–ACJ*, *z*, and that of the tetrahedron *P–HKM*, *t*. Now it is a geometrical property of the regular tetrahedron that the sum of the edges of these four smaller tetrahedra, $x + y + z + t$, is equal to the edge of the large tetrahedron, and the following method for the graphical representation of the quaternary mixture can therefore be deduced.[1] The four components, W, S_1, S_2, and S_3, are represented by four points in space, situated at the vertices of a regular tetrahedron the edge of which is equal to 100. A point P inside the tetrahedron represents a mixture of the four components, and the weight percentage of S_1 contained in this mixture is measured by the distance of P from the tetrahedral face WS_2S_3, *i.e.*, the face opposite to the S_1 vertex, in a direction parallel to either of the three edges not contained by this face; it is, in other words, measured by the length, x, of the edge of the small tetrahedron P–DFL. Similarly, the weight percentage of S_2 contained in the mixture is measured by the distance of P from the face WS_1S_3, opposite to the S_2 vertex, in a direction parallel to either of the three edges not contained by this face; it is therefore given by the length, y, of the edge of the small tetrahedron P–BEG. Finally, the weight percentage of S_3 is measured by the distance of P from the face WS_1S_2, opposite to the S_3 vertex, in a direction parallel to either of the three edges not contained by this face; it is therefore given by the length, z, of the edge of the small tetrahedron P–ACJ. These three distances, x, y, and z, will suffice to fix the position of P in space, and when it has been so fixed, then the distance t of the point from the face of $S_1S_2S_3$ opposite to W, measured in a direction parallel to WS_1, WS_2, or WS_3, gives the weight percentage of water in the mixture which is represented by P; for we have shown above that

$$x + y + z + t = S_2S_3 = 100,$$

and therefore $$t = 100 - \overline{x + y + z}.$$

This representation is, therefore, symmetrical with respect to each of the four components. The concentration of each component in a quaternary mixture finds expression in the figure, and each is similarly measured by the distance of the point representing the mixture from the face opposite to the vertex which denotes the particular component, in directions parallel to the edges of the tetrahedron.

§ 50. Let us consider a point such as A on the face WS_2S_3 of the tetrahedron (Fig. 71). Since this point lies on the face opposite to S_1, its distance from that face is zero, and the point represents, therefore, a mixture containing none of the component S_1. The percentage weight of S_2 contained in the mixture represented by A is given, in accordance with the method of representation described above, by AB or AC, the distance of the point A from the face WS_3S_1 opposite to S_2, measured parallel to S_2W or to S_2S_3. The percentage weight of S_3 contained in the mixture represented by A is similarly given by AD or AE, and that of water by AF or AG. We see, therefore, that a point such as A on the tetrahedral face WS_2S_3 represents a ternary mixture of W, S_2, and S_3, and the composition of this ternary mixture is defined in the usual way by the distance of the point from the three sides of the triangle WS_2S_3 in directions parallel to those sides.

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[1] From the construction in Fig. 70, it can be seen that
$x+y+z+t=PF+PB+PA+HK=HR+KQ+HN+HK=HR+NQ=S_2S_3$.

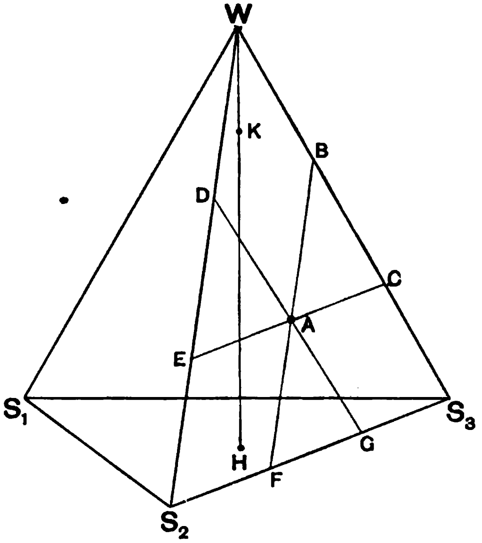


FIG. 71.

In the same way, points on the face WS_1S_2 represent ternary mixtures of W,S_1, and S_2, points on the face WS_3S_1, ternary mixtures of W, S_3, and S_1, and points on the face $S_1S_2S_3$, ternary mixtures of S_1, S_2, and S_3.

A point such as E, on the edge WS_2 of the tetrahedron, lies on both the faces WS_1S_2 and WS_2S_3, and represents, therefore, a mixture containing neither of the components S_1 and S_3, which are denoted by the vertices opposite to these faces. The

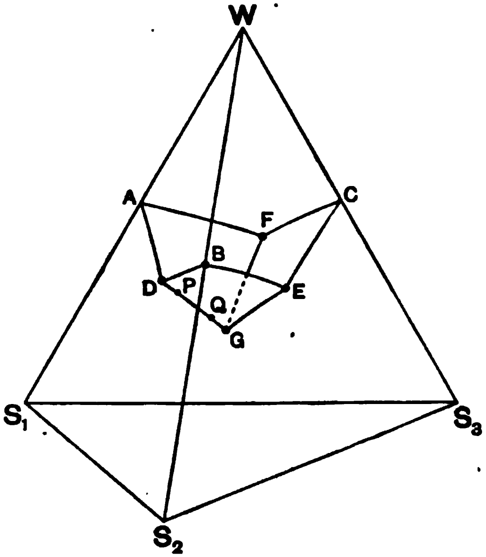


Fig. 72.

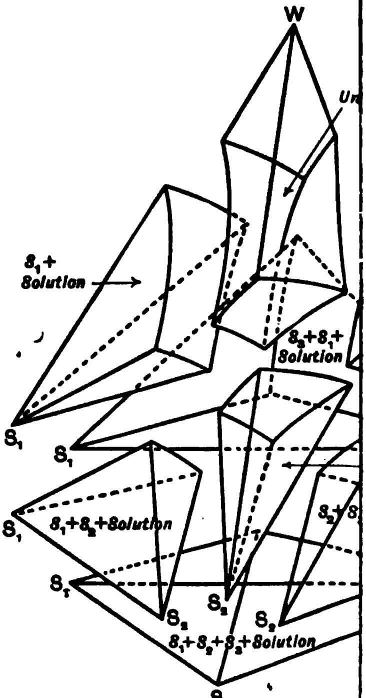


Fig. 74.

SHEET IX.

percentage weight of S_2 contained in the mixture represented by the point E is measured by WE, its distance from the face WS_3S_1, and the percentage weight of W by ES_2, its distance from the face $S_1S_2S_3$. Hence points on the edge WS_2, represent binary mixtures of W and S_2, the percentage by weight of each of the two components in the mixture being measured in the usual way by the lengths of the sections into which the line WS_2 is divided by the point. In the same way, points on each of the other five edges represent binary mixtures of the two components denoted by the corresponding end-points. Summarising, we see that if the four corners of a regular tetrahedron represent four pure components, then points on the six edges represent all possible mixtures in the six binary systems formed from the four components by taking them in pairs, points on the four faces represent all possible mixtures in the four ternary systems formed from the components by taking three at a time, and points in the space within the tetrahedron represent all possible mixtures of the four components in the quaternary system.

Deductions may be made from the graphical representation of quaternary mixtures inside a regular tetrahedron which are precisely analogous to those which resulted from the representation of ternary mixtures inside an equilateral triangle. It can be proved by purely geometrical considerations that if two points R and S, referred to the tetrahedron, represent two quaternary phases or complexes, then any mixture of the two is represented by a point on the line RS; and further that the point representing the mixture divides the joining line into two sections the lengths of which are proportional to the amounts of the two phases or complexes contained in the mixture (*cf.* § 23).

[It is proved in solid geometry that if the positions of two points, R and S, in space are defined by their co-ordinates x_1, y_1, z_1, and x_2, y_2, z_2 referred to any three axes, then the co-ordinates of a point P on the straight line RS are

$$\frac{ax_1+bx_2}{a+b}, \quad \frac{ay_1+by_2}{a+b}, \quad \frac{az_1+bz_2}{a+b},$$

where a and b are the lengths of the sections into which the line RS is divided by the point P.]

For example, a point H on the base $S_1S_2S_3$ of the tetrahedron in Fig. 71 represents a ternary mixture containing S_1, S_2, and S_3. If water be added to this mixture, then the resulting quaternary phase or complex is represented by a point on the line *WH*. Conversely, the point *K* represents a quaternary mixture, and if water be continuously removed from it, as for example, by evaporation, then the point representing its composition will move along the line *WH* in the direction of *H*, and a dry salt mixture of the composition represented by *H* will be finally obtained.

§ 51. We will first assume that, in the system W–S_1–S_2–S_3, only the components can appear as solid phases, *i.e.*, that no binary or ternary compound exists, and we shall denote the pure components by the vertices of the regular tetrahedron $WS_1S_2S_3$ (Fig. 72). We must consider first the ternary and binary systems which form the limiting cases in the quaternary system when the concentration of one or two of the components is zero. At the fixed temperature *T*, there is one saturated solution in the binary system W–S_1 which is in equilibrium with the solid salt S_1; its composition is given by the point *A* on the edge WS_1. The point *B* on the edge WS_2 gives the composition of the binary solution saturated with S_2 at the temperature *T*, and the point *C* on the edge WS_3 gives the composition of the binary solution saturated with S_3 at the same temperature. We suppose that this temperature is so far below the melting points of the salts that all anhydrous salt mixtures are solid. In this case, no solution will be represented on the edges S_1S_2, S_2S_3, S_3S_1 or on the face $S_1S_2S_3$.

At the temperature *T* there will be but one solution saturated with $S_1 + S_2$ in the ternary system W–S_1–S_2. Its composition is represented by the point *D* on the face WS_1S_2, whilst *AD* and *BD* are the ternary saturation curves of S_1 and of S_2 respectively. The point *E* on the face WS_2S_3, represents the composition of the solution saturated with $S_2 + S_3$ in the ternary system W–S_2–S_3 at the temperature *T*, and *BE* and *CE* are the ternary saturation curves of S_2 and of S_3 in this system. The point *F* on the face WS_3S_1, gives the composition of the solution saturated at this temperature, with $S_3 + S_1$ in the ternary system W–S_3–S_1; *CF* and *AF* are the ternary saturation curves of S_3 and S_1 respectively, in this system.

The point D represents, as we have seen, a ternary solution saturated with $S_1 + S_2$. Suppose now that, to an unsaturated solution formed by dissolving a small quantity of S_3 in water, such quantities of the other two salts S_1 and S_2 are added that excess of each remains over, in stable contact with solution, when equilibrium has been attained. The resulting quaternary solution will be represented by a point such as P inside the tetrahedron. The distance of the point P from the face WS_1S_2, opposite to S_3, will be a measure of the amount of S_3 contained in the solution, whilst the distance of the point from the faces WS_2S_3 and WS_3S_1 will measure the percentages of S_1 and S_2 contained in the quaternary solution saturated with these two salts; the addition of S_3 will, in general, cause these to differ from the corresponding values for the ternary solution D, which is saturated with the same two salts. If more S_3 be added, the solution still remaining, however, unsaturated with respect to this salt, but saturated with respect to $S_1 + S_2$, then its composition will be represented by a different point, such as Q, further removed from the face WS_1S_2. Proceeding in this way, we obtain a series of points lying on a curve which is characterised by the fact that its every point represents a solution saturated, or in equilibrium, with the two solid salts S_1 and S_2; it is the quaternary isothermal saturation curve of $S_1 + S_2$. We have already given the proof (§ 48) that quaternary solutions saturated with two solids must be represented by points on such an isothermal saturation curve. This curve will clearly end in a point which represents a solution saturated with respect, not only to the two salts S_1 and S_2, but also with respect to the third salt, S_3. This solution is represented in Fig. 72 by the point G; since the solution G is in equilibrium with the three solid salts, it must be an isothermal invariant solution (§ 48). It is the only solution which is saturated, at the temperature T, with $S_1 + S_2 + S_3$.

In the same way, the point E, representing the ternary solution saturated with $S_2 + S_3$, must form the starting point of a quaternary saturation curve EG every point of which represents a quaternary solution saturated with $S_2 + S_3$. This curve must also end in the isothermal invariant point G, which represents the solution saturated with all three salts $S_1 + S_2 + S_3$. Finally, the curve FG, which starts from the ternary invariant point *F* and ends in the quaternary invariant point *G*, is the saturation curve of $S_3 + S_1$.

Quaternary solutions saturated only with the salt S_1 are represented by points on a surface which is bounded by the four curves the points of which also represent solutions saturated with this salt. These are the two ternary saturation curves *AD* and *AF*, and the two quaternary saturation curves *DG* and *FG* (which represent solutions saturated, not only with S_1, but also with a second salt, S_2 or S_3). The surface *ADGF* is the saturation surface of S_1; *BDGE* is, similarly, the saturation surface of S_2, and *CEGF* the saturation surface of S_3.

The isotherm contains, therefore, three saturation surfaces, the points of which represent solutions saturated with one salt.

ADGF is the saturation surface of S_1,
BDGE ,, ,, ,, S_2,
CEGF ,, ,, ,, S_3.

These saturation surfaces, intersecting in pairs, give rise to three saturation curves, the points of which represent solutions saturated with two salts.

DG is the saturation curve of $S_1 + S_2$,
EG ,, ,, ,, $S_2 + S_3$,
FG ,, ,, ,, $S_3 + S_1$.

All the saturation surfaces and curves intersect in one point, representing the solution saturated with all three salts.

G is the saturation point of $S_1 + S_2 + S_3$.

§ 52. We must next consider the meaning of points inside the tetrahedron, which lie neither on saturation curves nor on saturation surfaces. Points on the surface *BDGE* (Fig. 73) represent, as we have seen, solutions saturated with the salt S_2, and every point on this surface may therefore be joined by a conjugation line to the S_2 vertex. A pyramid is thus formed the apex of which is the vertex S_2, and the base is the saturation surface *BDGE*. A point within this pyramid represents a phase complex of solid S_2 and a solution on the saturation surface; it is called the two-phase space S_2–Solution. The pyramid can be distinguished more clearly in Fig. 74, in which the tetrahedron is dissected into the various complex spaces.

There clearly exist two other two-phase spaces in the tetrahedron. Any point inside the pyramid S_3–$CEGF$ (Figs. 73 and 74) represents a phase complex of solid S_3 and a solution on the saturation surface $CEGF$; any point inside the pyramid S_1–$ADGF$ represents a phase complex of solid S_1 and a solution on the saturation surface $ADGF$.

The point D represents the ternary solution saturated with $S_1 + S_2$, and points in the triangular area DS_1S_2 represent the ternary phase complexes $S_1 + S_2 +$ Solution. If, beginning from the ternary solution D, increasing amounts of the third salt S_3 are added to the solution, which remains in equilibrium with the two salts $S_1 + S_2$, the point which represents, in its successive positions, the compositions of the resulting quaternary solutions will move along the saturation curve from D to G, and the area DS_1S_2, the points of which represent the complexes $S_1 + S_2 +$Solution, will generate the three phase space S_1–S_2–Solution. This space forms a tetrahedron the vertices of which are D, G, S_1, and S_2; two of the faces of this tetrahedron, namely, DS_1S_2 and GS_1S_2, are plane triangles, but the other two, S_1DG and S_2DG, are, in general, sectors of a conical surface. This space can be more clearly distinguished in Fig. 74. There are two other three-phase spaces in the quaternary isotherm, and these are generated in a similar way. The tetrahedron EGS_2S_3 is the three-phase space S_2–S_3–Solution, and the tetrahedron FGS_3S_1 is the three-phase space S_3–S_1–Solution.

The point G represents the quaternary solution which is in equilibrium with the three solid salts S_1, S_2, and S_3; points in the tetrahedron $GS_1S_2S_3$, the apex of which is the point G and the base of which is the triangle $S_1S_2S_3$, represent complexes of solid S_1, solid S_2, solid S_3, and the invariant solution G; this space is called the four-phase space S_1–S_2–S_3–Solution.

Finally, points in the space above the saturation surfaces represent mixtures which do not contain sufficient of the salts to form a saturated solution. It is therefore the space of unsaturated solutions. It will be found that the eight spaces enumerated comprise the whole of the interior of the component tetrahedron $WS_1S_2S_3$. In addition to the saturation curves and surfaces, there are three two-phase spaces, three three-phase spaces, one four-phase space, and one space of unsaturated solutions.

§ 53. The representation inside a regular tetrahedron gives, as we see, a good qualitative survey of the isothermal conditions of equilibrium in the quaternary system. It would, however, be very difficult to represent actual quantitative analytical results in this way. For the latter purpose, a plane projection of the space figure may be constructed, and in order to reconstruct the space figure, two such projections will clearly be necessary, for example, a projection upon a horizontal plane and one upon a vertical plane. The two projections which reproduce the features of the space figure most clearly are those which have been used by Schreinemakers to represent the results of his investigations on quaternary equilibria.

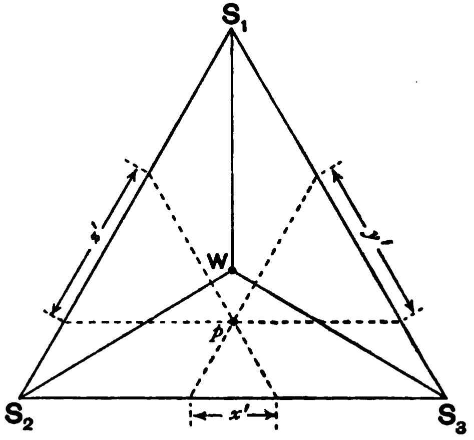


Fig. 75.

In the first method of Schreinemakers, the tetrahedron and the space figure contained within it are projected upon the base of the tetrahedron by means of parallel lines perpendicular to the base. The triangle $S_1S_2S_3$ of Fig. 75 represents the base of the tetrahedron drawn in the plane of the paper.

The vertex of the tetrahedron, which represents pure water, projects into a point upon the base perpendicularly below it, and this point is clearly given by the centroid W of the triangle $S_1S_2S_3$ in the projection (Fig. 75). The three edges WS_1, WS_2, and WS_3 project into parts of the three medians of the triangle $S_1S_2S_3$, and the three tetrahedral faces WS_1S_2, WS_2S_3, and WS_3S_1 project into the corresponding isosceles triangles in Fig. 75.

When the typical quaternary isotherm which we discussed in the previous paragraph is projected in this way upon the base of the tetrahedron, a figure is obtained similar to that shown in Fig. 76. The points *a*, *b*, and *c* (Fig. 76) are the projections of the points *A*, *B*, and *C* (Fig. 72) which give the compositions of the binary saturated solutions. They lie on the medians WS_1, WS_2, WS_3 of the triangle $S_1S_2S_3$, since these medians are, as we have seen, the projections of the corresponding edges of the tetrahedron.

The three ternary systems are now represented inside the triangles WS_1S_2, WS_2S_3, and WS_3S_1 (Fig. 76), which are the projections of the tetrahedral faces; *ad* and *bd* give, therefore, the ternary saturation curves of S_1 and of S_2 in the system W–S_1–S_2, *be* and *ce* the ternary saturation curves of S_2 and of S_3 in the system W–S_2–S_3, and *cf* and *af* those of S_3 and of S_1 in the system W–S_3–S_1. The point *g* is the projection of the quaternary invariant point *G*, whilst *dg*, *eg*, and *fg* are the quaternary saturation curves of $S_1 + S_2$, of $S_2 + S_3$, and of $S_3 + S_1$, respectively. It can be seen very clearly from the projection that these curves are formed by the intersections of the saturation surfaces, *adgf* that of S_1, *bdge* that of S_2, and *cegf* that of S_3.

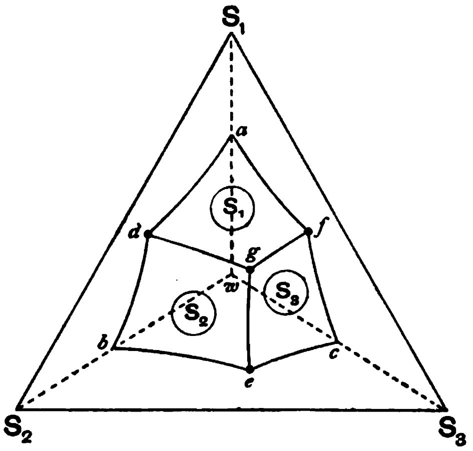


FIG. 76.

In order to construct such a projection as that shown in Fig. 76 from actual exerimental data, it is clearly necessary to know the relation which exists between the position of a point in the tetrahedron and that of its projection in the triangular base. The position of any point *P* within the tetrahedron has already been defined by *x*, *y*, *z*, and *t*, the percentages of the four components S_1, S_2, S_3, and *W* contained by the quaternary mixture which *P* represents (§ 49). The position of its projection *p* (Fig. 75) we can define in the usual way by the distances of *p* from the three sides S_2S_3, S_3S_1, and

S_1S_2 of the triangular base, measured in directions parallel to those sides. We will call these three distances x', y', and z', respectively. The point p is, actually, the projection of a point in space which represents a quaternary mixture, but if we suppose for the moment that, in virtue of its position within the triangle $S_1S_2S_3$, it represents a ternary mixture with the three salts as components, then the distances x', y', and z' would give the percentage of S_1, S_2, and S_3, respectively, contained by this ternary mixture. The relations which exist between x, y, z, and t on the one hand and x', y', and z' on the other can be obtained from purely geometrical considerations. They are:

$$x' = x + t/3,$$
$$y' = y + t/3,$$
$$z' = z + t/3.$$

The position of the projection p of a point representing a quaternary mixture of the known percentage composition

$$xS_1, yS_2, zS_3, tW,$$

is therefore determined by the following simple rule.

The actual percentage (x) of S_1 in the quaternary mixture is increased by one-third the percentage of water ($t/3$) in that mixture, and the percentages (y and z) of S_2 and of S_3 are each increased by the same amount.

The point in the triangle $S_1S_2S_3$ which would represent a ternary mixture of S_1, S_2, and S_3 of the composition given by these new values:

$$(x + t/3)S_1, (y + t/3)S_2, (z + t/3)S_3,$$

gives the position of the desired projection on the base of the tetrahedron.

§ 54. The second projection which is used by Schreinemakers is obtained in the following way:

The base $S_1S_2S_3$ of the tetrahedron represented in Fig. 72 is supposed to rest upon the ground plane, and the vertex W is then perpendicularly above the centroid of the base triangle $S_1S_2S_3$. Suppose now that the tetrahedron with its space figure is rotated about the edge S_2S_3, which remains upon the ground plane, until the other two vertices S_1 and W are equidistant above that plane and the edge S_1W is, therefore, parallel to it.

The tetrahedron alone is represented in this position by Fig. 77, and it is now projected upon the ground plane by means of lines perpendicular to that plane, as indicated by the dotted lines in the figure. The line s_1w is the projection of the tetrahedral edge S_1W, and since this edge is parallel to the ground plane, its length will not be altered by the perpendicular projection; s_1w is therefore equal to S_2S_3 in length, and these two lines, from the symmetry of the figure, must clearly bisect one another at right angles. Hence the lines s_1w and S_2S_3 form the diagonals of a square $wS_2s_1S_3$, and the four sides of this square are evidently the projections of the remaining four edges of the tetrahedron.

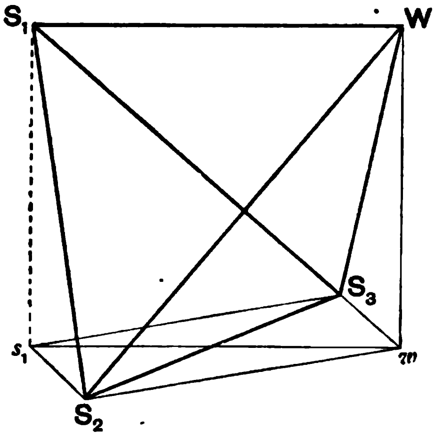


Fig. 77.

The typical isotherm of Fig. 72 is represented in this projection by Fig. 78. The sides of the square $WS_2S_1S_3$ and its two diagonals are the projections of the six edges of the tetrahedron reproduced in the plane of the paper from Fig. 77. The three ternary systems are represented inside the three triangles WS_1S_2, WS_2S_3, and WS_3S_1, which are the projections of the three corresponding faces of the tetrahedron. As before, *ad* and *bd*, *be* and *ce*, *cf* and *af* are ternary saturation curves, whilst *dg*, *eg*, and *fg* are quaternary saturation curves,

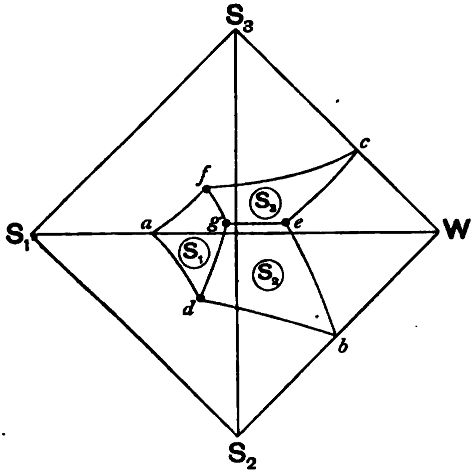


Fig. 78.

and the point g is the quaternary invariant point. The saturation surfaces, which represent solutions saturated with one salt, are marked in the figure with their corresponding solid phases. Here again, in order to construct the projection from experimental results, we must know the relation which exists between the position of a point P inside the tetrahedron and that of its projection p inside the square. The position of P in the tetrahedron is defined, as before, by the four concentrations x, y, z, and t. We can define that of its projection p inside the square (Fig. 79) by the distances of p from the diagonals S_1W and S_2S_3, which can then be regarded as axes of co-ordinates. If the distance pb of the point p from the axis S_2S_3 is called a, and its distance pd from the axis S_1W is called b. then we must know the relations which exist between x, y, z, and t on the one hand, and a and b on the other. These relations, which are purely geometrical, are :

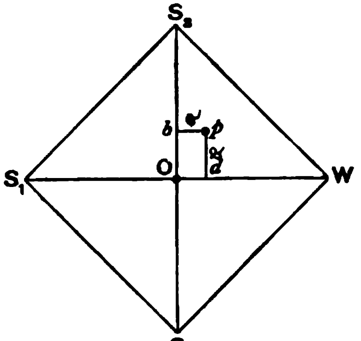


FIG. 79.

$$a = \frac{t - x,}{2}$$

$$b = \frac{z - y.}{2}$$

The position, in this picture, of the point which represents the quaternary mixture the composition of which is xS_1,yS_2, zS_3,tW can therefore be found in the following way. The lines OW and OS_3 (Fig. 79) are taken as axes, and the coordinates a, b of the required point, referred to these axes, are calculated by means of the relations given above. The co-ordinate a is measured parallel to the axis OW, and it is equal to half the difference between the concentrations (t and x) of the two components (W and S_1) which are represented on this axis. The co-ordinate b is measured parallel to the axis OS_3, and it is equal to half the difference between the concentrations (z and y) of the two components (S_3 and S_2) which are represented on it. Due regard must, however, be paid to the algebraic sign of these co-ordinates. Thus $t - x$ will be negative if the concentration of the salt S_1 is greater than the concentration of water,

and in this case the distance $\frac{t - x}{2}$ must be measured parallel to the axis OW, but in a negative direction, *i.e.*, in the direction from O to S_1; the point will then lie in the left half of the picture. Similarly, if $\frac{z - y}{2}$ is negative, it must be measured in the direction of OS_2 and the point will lie in the lower half of the picture.

In the foregoing description, we have supposed the two opposite tetrahedral edges WS_1 and S_2S_3 to be projected into the diagonals of a square upon the ground plane, but clearly any pair of opposite edges could be so projected by a suitable arrangement of the tetrahedron. Thus by keeping the edge S_3S_1 of the tetrahedron represented in Fig. 72 upon the ground plane, and rotating the tetrahedron until the edge WS_2 is parallel to this plane, we should be in a position to project these two edges (S_3S_1 and WS_2) into the diagonals of a square upon the ground plane. In a similar way, the opposite edges, S_1S_2 and WS_3, might be made the diagonals of a square, but in any of these cases the point in the projection which represents the composition of a certain quaternary mixture is determined by the rule which we have given above; the co-ordinates of the point, referred to the diagonals as axes, will be equal to half the difference between the concentrations of those components in the quaternary mixture which are denoted by opposite corners of the square.

§ 55. The behaviour of various mixtures on the isothermal addition or removal of water is more complicated than was the case in the ternary system, but it can be studied by similar methods. Let us first consider an unsaturated solution which is represented by a point such as T, within the space of unsaturated solutions (Fig. 80). On the isothermal evaporation of water from the solution T, it will, at first, remain unsaturated, and its composition will be represented by a point which moves along the straight line WR from T in the direction of R. This condition will continue until the solution attains the composition given by the point Q, where the line WR intersects the saturation surface of S_1.

At this point, the solution will become just saturated with respect to the salt S_1, and further evaporation of water must therefore result in the deposition of this salt. A series of solutions will then be obtained all saturated, or in equilibrium, with solid S_1. The path traced out by the point representing the composition of the solution during this stage of the evaporation must therefore lie on the saturation surface $ADGF$, and its exact position is determined by the following considerations.

Since the salt S_1 is alone deposited, the proportion of the salt S_2 to the salt S_3 contained by the solution must remain constant during this stage of the evaporation, and equal to the proportion of S_2 to S_3 contained by the original unsaturated solution T. Now we have shown in § 50 that the composition of the *salt mixture* contained by the unsaturated solution T is given by the point R in which line the WT produced intersects the base of the tetrahedron. The point R represents a ternary mixture of the three salts S_1, S_2, and S_3, and it contains the two salts S_2 and S_3 in a proportion given by the point H in which the line S_1R produced intersects the side S_2S_3 of the triangle $S_1S_2S_3$ (*cf.* § 23). The point H gives, therefore, the proportion of the salt S_2 to the salt S_3 contained by the unsaturated solution T. All quaternary mixtures which can be formed by bringing together the binary mixture H, the salt S_1 and water are represented by points in the triangle HS_1W or, in other words, all quaternary mixtures which contain the two salts S_2 and S_3 in the constant proportion given by H (and therefore also by T) are represented by points on the triangular section HS_1W of the tetrahedron. We have shown above, however, that when water is evaporated from the saturated solution Q solid S_1 separates, the proportion of S_2 to S_3 contained by the solution remains unchanged, and the point representing the composition of the solution traverses a path on the saturation surface $ADGF$. It follows, therefore, that this path must be the line of intersection of the surface with the triangular section HS_1W of the tetrahedron. This line of intersection is given by the curve AL in Fig. 80; it is one of the paths of crystallisation on the saturation surface of S_1. When so much water has been evaporated that the composition of the solution is represented by the point L, which lies on the quaternary saturation curve FG, the solution will become saturated with a second salt, namely, with the salt S_2. The continued evaporation of water will therefore cause the separation of this salt together with S_1, and the point representing the composition of the solution will now follow the curve FG, the points of which give the compositions of all solutions saturated with the two salts S_1 and S_3. When the composition of the solution has reached the value given by the point G, the solution itself will be just saturated with the third salt S_2. Further evaporation of water will therefore cause the separation of solid S_2, and since the solution is now in contact with the three solid salts, its composition will no longer alter. It will dry completely at the constant composition given by G, with the simultaneous separation of all three salts. The point G is, therefore, the quaternary drying-up point.

We will now suppose that the position of the point T can vary, and we will assume first that the line WT produced still intersects the saturation surface of S_1, but that the proportion of the two salts S_2 to S_3 contained by the solution T is given by the point P instead of by the point H. The path of crystallisation on the saturation surface of S_1 will now be given by the curve of intersection AM, of the triangular section PS_1W, with the surface. We may say, quite generally, that the paths of crystallisation on the saturation surface of S_1 are given by curves which radiate from the point A and end on a quaternary saturation curve; these paths are the intersections, with the saturation surface, of all possible triangular sections of the tetrahedron which pass through the edge WS_1.

The position of the point T in the space of unsaturated solutions may, however, be such that the line WT produced intersects the saturation surface $CEGF$ of S_3. In this case, the unsaturated solution T will become saturated first with the salt S_3, when water is evaporated from it, and the path of crystallisation during the separation of solid S_3 will be given by a curve on the saturation surface of S_3. It can be shown by the method which we have already used that the paths of crystallisation on the saturation surface of S_3 are curves which all radiate from the point C, and which are formed by the intersection, with the surface, of all triangular sections which pass through the edge WS_3.

In exactly the same way, the paths of crystallisation on the saturation surface of S_2 are curves which radiate from the point B, and which are formed by the intersection, with this surface, of all triangular sections which pass through the edge WS_2.

The projection of the typical quaternary isotherm upon the base of the tetrahedron (§ 53) is shown in Fig. 81, and the paths of crystallisation are marked. On the saturation surfaces these paths are given by lines which radiate from the points *a*, *b*, and *c*. These lines are, strictly, not straight, although they are so represented in Fig. 81. They are the projections of curves such as *AL* and *AM* in Fig. 80 ; the projection is made by means of lines perpendicular to the base, and since the triangular sections HS_1W, PS_1W, which contain the curves *AL* and *AM* are not, in general, perpendicular to the base, they will not contain the perpendicular projecting lines. The projections of the paths *AL* and *AM* will, therefore, still be curves and not straight lines.

The directions in which the point representing the compositions of solutions traverses the paths of crystallisation are indicated by the arrow-heads in Fig. 81. The quaternary saturation curves *dg*, *eg*, and *fg* are themselves paths of crystallisation, and the invariant point *g* is the quaternary drying-up point.

§ 56. The quaternary isotherm can be represented in a slightly different form by the method of Jänecke. For the purpose of Jänecke's representation, we have seen that it is necessary to refer the concentrations of the components in the liquid phase to 100 parts by weight of the total salts in that phase, instead of 100 parts by weight of the whole solution. The composition of a quaternary solution must therefore be expressed in the form

$$mW, xS_1, yS_2, (100 - \overline{x + y})S_3,$$

where the sum of the concentrations of the three salts S_1, S_2, and S_3 is constant, and equal to 100. This expression for the composition of a quaternary solution contains the three varying factors m, x, and y, and the isothermal conditions of equilibrium can, therefore, still be represented graphically only by means of a space figure. We can, however, obtain a partial representation of the quaternary isotherm in one plane if we omit the expression of the water content m. The simultaneous variations of x with y can be represented in a plane figure, and if these two variables are referred to the two sides of an equilateral triangle in the usual way, then the dependent variable $100 - \overline{x + y}$ also receives actual graphical expression.

The resulting figure will show the percentage composition,

$$xS_1, yS_2, (100 - \overline{x + y})S_3,$$

of the salt mixture contained in a given saturated solution, but it will give no information concerning the water content *m* of the solution. The simple quaternary isotherm which we have already discussed is represented in this way by Fig. 82. The point *g* in this figure gives the composition of the salt mixture contained in the isothermal invariant solution, and it is the common point of intersection of the three saturation curves. The curve *dg* is the saturation curve of the two salts $S_1 + S_2$, and it ends in the point representing the composition of the salt mixture contained in the ternary invariant solution which is also saturated with these two salts. This point must clearly lie on the side S_1S_2, since the ternary invariant solution contains these two salts only ; it is the point *d* of Fig. 82. The curves *eg* and *fg* are the saturation curves of $S_2 + S_3$ and of $S_3 + S_1$, respectively, and they end in the points *e* and *f*, which represent the compositions of the salt mixtures contained in the ternary invariant solutions which are in equilibrium with $S_2 + S_3$ and $S_3 + S_1$, respectively.

This partial representation of the quaternary isotherm can also be considered as a plane projection of the complete isotherm which is represented within the tetrahedron in Fig. 72. We have already described two parallel projections of this space figure (§§ 53 and 54), *i.e.*, projections produced by parallel lines—in the cases considered, lines which were all perpendicular to the plane of projection. Suppose now that the space isotherm is projected upon the base of the tetrahedron by means of lines which all radiate from the vertex *W*, as shown by the dotted lines in Fig. 83. This will give us, not a parallel, but a perspective projection, in which *W* is the vertex of perspection. The point *D* (Fig. 83) on the face WS_1S_2 will clearly project into a point *d* on the edge S_1S_2, the point *E* into the point *e* on the edge S_2S_3, and the point *F* into the point *f* on the edge S_3S_1. The quaternary invariant point *G* will project into a point *g* within the triangle $S_1S_2S_3$, and the quaternary saturation curves *DG*, *EG*, and *FG* will project into the curves *dg*, *eg*, and *fg* in the base triangle. We have, however, shown in § 50 that a point such as *g* (Fig. 83), formed by the intersection of the line *WG* produced, with the base of the tetrahedron, gives the composition of the salt mixture contained in the solution represented by *G*. The projection shown on the base of the tetrahedron in Fig. 83 is, therefore, identical with Jänecke's representation shown in Fig. 82. This method of representation possesses one important advantage which the projections of §§ 53 and 54 do not. We showed in the previous paragraph that the paths of crystallisation, for example, on the saturation surface of S_1, were formed by the intersections, with the surface, of triangular sections of the tetrahedron through the edge WS_1. In the perspective projection of Fig. 83 these paths will be projected upon the base of the tetrahedron by means of lines which radiate from *W*, and which are, therefore, contained by the triangular sections themselves. It follows that the paths of crystallisation on the saturation surfaces will project into straight lines on the base of the tetrahedron. they are, therefore, correctly represented as straight lines in Fig. 82.

We see that, as in the case of the ternary polytherm (§ 38), so too in the case of the quaternary isotherm, we can consider Jänecke's method of representation from two points of view. We can regard it as the projection of a figure which involves an additional space dimension, and which more completely depicts the system. We can, on the other hand, consider the concentration variables as separated into that variable which gives the water content of saturated solutions, and those variables which give the composition of the salt mixture contained by saturated solutions. Jänecke's graphical representation is then obtained by treating these variables independently.

It can be seen from a comparison of Figs. 81 and 82 that a close similarity exists between Jänecke's representation of the quaternary isotherm and the projection of the space figure which was described in § 53. This arises from the fact that both figures can be obtained by projecting the space isotherm upon the base of the tetrahedron, the former by means of lines perpendicular to the base, and the latter by means of lines radiating from the vertex W. They differ only in the fact that, whereas the ternary saturation curves appear within the triangle $S_1S_2S_3$ of Fig. 81, these curves project actually into the sides S_1S_2, S_2S_3, and S_3S_1 of the triangle $S_1S_2S_3$ of Figs. 82 and 83.

§ 57. We have seen that the composition of a quaternary liquid involves three independently variable factors. The conditions of equilibrium at a fixed temperature could only be represented completely by a figure of three dimensions, *i.e.*, by a space figure. If now we allow the temperature to vary, it must be considered as a fourth variable, and we should therefore require a figure of four dimensions in order to depict graphically all the conditions of equilibrium. Since such a figure exists only as a mathematical abstraction, we are unable to obtain a complete representation.

The composition of a quaternary liquid, expressed by Jänecke's method, is given in the form

$$mW, xS_1, yS_2, (100-\overline{x+y})S_3,$$

containing the variables m, x, and y, with which we must now include the fourth variable T. By referring the two independent variables x and y, and the dependent variable $100 - \overline{x + y}$, to the sides of an equilateral triangle, we were able to obtain a partial representation of the quaternary isotherm in one plane. If in a second plane, perpendicular to the first, we measure the water content m of solutions saturated at a fixed temperature, then we shall obtain a space figure which represents the complete isothermal equilibrium conditions within a triangular prism, in place of the regular tetrahedron which we have previously used. We may, however, as an alternative, neglect the variable m, and measure instead the temperature T in the second plane. We can, in this way, represent the effect of temperature change upon the composition of the salt mixtures contained in saturated solutions ; the representation will be incomplete, since it will take no account of the water content of solutions. The conditions of equilibrium in the quaternary system W–S_1–S_2–S_3 are represented in Fig. 84 within a triangular prism, at all temperatures where solutions may exist. We assume here that the salts suffer no decomposition by water, that two liquid layers are not formed, and that the critical temperature of mixtures is not reached. A point on a saturation curve or surface of this figure represents a solution of the salt mixture the composition of which is given by the distance of the point from the three sides of the horizontal triangular section in which it lies. The temperature of the solution is given by the perpendicular distance of this section above the base $S_1S_2S_3$ of the prism, which is considered as lying in a horizontal plane; the temperature is, therefore, measured parallel to either of the three vertical edges of the prism. We must first consider the three fundamental ternary systems which are represented, one on each of the three vertical prismatic faces. Since no binary or ternary compounds are supposed to exist, these systems are all of the type represented by Fig. 43 in a previous chapter. The system W–S_1–S_2 at varying temperatures is shown in the face AS_1S_2B. The points A and B are the melting points of the pure salts, and the point D is the eutectic point in the binary salt system S_1–S_2. This latter system is *completely* represented by the two binary saturation curves AD and BD of S_1 and S_2, since the water content is here actually zero. The points G and H represent the eutectic points in the two binary systems W–S_1 and W–S_2, and K is the ternary eutectic point where the three solids S_1, S_2, and Ice are in equilibrium with an invariant solution in the system W–S_1–S_2. From this point, three ternary polythermal saturation curves radiate in the direction of rising temperature, KG that of Ice + S_1, KH that of Ice + S_2 and KD that of $S_1 + S_2$. The last extends continuously to the eutectic point D in the binary salt system, where solid S_1 and solid S_2 are both in equilibrium with an anhydrous melt. Identical with this in type are the other two systems W–S_2–S_3 and W–S_3–S_1, represented on the corresponding faces.

The ternary system S_1–S_2–S_3 is represented by the space figure $ADBECFN$. It is also identical in type with the other ternary systems, but since it is represented completely (water being absent, the concentrations of all its components receives graphical expression), it must be compared with the space figure depicted in Fig. 41 of a previous chapter, which gives the complete representation of equilibrium conditions in the system W–S_1–S_2. There exists no difference in type between the ternary system where water forms one component and the anhydrous ternary system such as S_1–S_2–S_3; the latter system will, in general, be more symmetrical than the former, since no such large difference will exist between the melting points of the three salts, as exists between those of ice and the two salts. Thus the point N represents the ternary eutectic melt in equilibrium with the three solids S_1, S_2, and S_3. The curve ND is the polythermal saturation curve of $S_1 + S_2$, NE that of $S_2 + S_3$, and NF that of $S_3 + S_1$ in the ternary system; the surfaces $ADNF$, $BDNE$, and $CENF$ are the ternary saturation surfaces of S_1, S_2, and S_3, respectively. We see that this ternary system receives a preferential treatment in the representation, in the same way that the anhydrous binary system receives a preferential treatment in Jänecke's representation of the ternary system (§ 38). The reason is the same in both cases, namely, since the system contains no water, the conditions of equilibrium are completely reproduced.

We can now consider the various quaternary saturation curves and surfaces which are represented in the interior of the prism. The point P is the system invariant point which represents the quaternary solution in equilibrium with the four solid components Ice, S_1, S_2, and S_3, (more strictly, it represents the composition of the salt mixture contained by this solution). We have seen that a system invariant point of this kind, whether binary, ternary or quaternary, is always a eutectic point (§ 18) On withdrawing heat from the invariant system, the constant composition of the liquid phase is maintained by a phase reaction which consists in the deposition of the four solid components in the same weight proportion as that in which they are contained by the quaternary liquid. On the addition of heat to the invariant system, the opposing phase reaction occurs, namely, the dissolution of the four solid components in this same proportion. These phase reactions are represented by the following scheme:

$$\text{Ice} + S_1 + S_2 + S_3 \rightleftarrows \text{Solution } P.$$

If heat is withdrawn from the system, the following phase reaction occurs:

$$\text{Solution } P \qquad \text{Ice} + S_1 + S_2 + S_3,$$

and the temperature will not fall until the liquid phase has been completely removed by this reaction. The point P gives the lowest temperature at which a liquid phase can exist in the system, and it is, therefore, the lowest point in the polytherm of Fig. 84. If heat be added to this invariant system, the temperature will not alter, but the following reaction will take place:

$$\text{Ice} + S_1 + S_2 + S_3 \rightarrow \text{Solution } P.$$

When, during the course of this reaction, one of the solid phases has been completely removed, then the system will gain a degree of freedom, the temperature will commence to rise, and we shall be left at higher temperatures with one of the four following monovariant systems:

$$\begin{aligned}&\text{Ice} + S_1 + S_2 + \text{Solution},\\ &\text{Ice} + S_1 + S_3 + \text{Solution},\\ &\text{Ice} + S_2 + S_3 + \text{Solution},\\ &S_1 \;\; + S_2 + S_3 + \text{Solution}.\end{aligned}$$

Four saturation curves must therefore radiate from the point P. The curve PK is the saturation curve of Ice + S_1 + S_2, and it ends in the ternary eutectic point K where these three solids are in equilibrium with the ternary eutectic solution. The curve PL is the saturation curve of Ice + S_2 + S_3, and it ends in the ternary eutectic point L; the curve PM is the saturation curve of Ice + S_3 + S_1 and it ends in the ternary eutectic point M. The curve PN is the saturation curve of S_1+S_2+ S_3; it has much the longest temperature range, extending continuously from the quaternary eutectic point P, where the three solid salts and ice are in equilibrium with solution, to the ternary eutectic point N where the three solid salts are in equilibrium with an anhydrous salt melt.

The condensed quaternary system formed by three solid phases in stable contact with a solution is a system in monovariant equilibrium (§ 48). If, however, we fix one of the equilibrium conditions—the temperature—the system then becomes invariant, as we have already seen. The polythermal saturation curve PN, which represents the monovariant system S_1–S_2–S_3–Solution, can therefore be considered as giving the locus, with varying temperature, of the isothermal invariant point which represents the solution in equilibrium with the three solid salts. Solutions saturated with two solids were represented in the isotherm by saturation curves, and, therefore, in the polytherm they are given by saturation surfaces which can be considered as generated by the isothermal curves when the temperature varies. The surface *DNPK* is the saturation surface of $S_1 + S_2$, bounded, as we see, by the four saturation curves—two ternary and two quaternary—which also represent solutions saturated with these two salts. Similarly, *ENPL* is the saturation surface of $S_2 + S_3$, and *FNPM* that of $S_3 + S_1$. In addition to these, there are three other saturation surfaces, representing solutions saturated with ice and one salt. The surface *GKPM* is the saturation surface of Ice + S_1, *HKPL* that of Ice + S_2, and *JMPL* that of Ice + S_3. The saturation surfaces bound spaces the points of which represent solutions saturated with one solid only. These spaces can be more clearly distinguished from Fig. 85, in which the model is dissected into the saturation spaces of S_1, S_2, and S_3.

The quaternary isotherms are given by plane sections of the space figure parallel to $S_1S_2S_3$, sections the points of which represent mixtures at one and the same temperature. In Fig. 84, *QRT* is such a section. It intersects the polythermal saturation curve *PN* in the point *g*, which represents, therefore, the isothermal invariant solution saturated with $S_1 + S_2 + S_3$. It intersects further the saturation surface of $S_1 + S_2$, of $S_2 + S_3$, and of $S_3 + S_1$, and the curves of intersection *dg*, *eg*, and *fg* are the corresponding saturation curves. Lastly, the surfaces *Qfgd*, *Rdge*, and *Tegf* are the intersections of the plane *QRT* with the three spaces which represent solutions saturated with one salt; they are the isothermal saturation surfaces of S_1, S_2, and S_3. The section gives, therefore, the isothermal type which we have already deduced, and which is represented in the plane of the paper in Fig. 82. This type obtains over a very wide range of temperature, namely, from the melting point of ice to the ternary eutectic point in the anhydrous system S_1–S_2–S_3. Other types occur at temperatures outside this range. Below 0°, ice may occur as a solid phase, and the quaternary isotherm must then contain a fourth saturation surface—that of ice. On the other hand, above the temperature of the ternary eutectic point in the system S_1–S_2–S_3, the three solids S_1, S_2, and S_3 cannot all remain in stable contact with liquid. The point N of Fig. 84 is the upper temperature limit of the saturation curve of $S_1 + S_2 + S_3$, so that above this temperature the isotherm can contain no quaternary isothermal invariant point. We do not propose to give a detailed description of the various isothermal types which may arise; they are very numerous, but they can all be deduced from Fig. 84. A transition form will exist at every melting point of a pure component, at every binary and ternary eutectic point, and at the quaternary eutectic point. There are therefore fifteen transition forms and a corresponding number of isothermal types. As we have seen, one of these types has a very much longer temperature range than the others. It is the type which we have already discussed at length. When, however, a binary compound can exist as a solid phase in the quaternary system, a series of very important isothermal types arises, which we shall consider in detail in the next paragraph.

§ 58. It must have already become evident that the classification of heterogeneous equilibria on the basis of the phase theory reveals a close analogy between the comparatively simple relations which obtain in the ternary system and the considerably more complex relations of the quaternary system. As the number of components in the system increases, so the possible variability of the system increases, and this is manifested by the increased number of phases necessary for the definition of invariant equilibrium, and the increased number of possible isothermal types.

We will suppose that a salt hydrate $S_1.x\mathrm{H_2O}$, which we will denote by H_1, can appear as a solid phase. We have seen that, in this case, the ternary system W–S_1–S_2, at a temperature sufficiently low, is of the simple type which shows only two isothermal saturation curves, those of the hydrate H_1 and the anhydrous salt S_2. At a temperature sufficiently high, the hydrate will be unable to exist, and the ternary isotherm will again be of the simplest type; it will show only the saturation curves of the two anhydrous salts S_1 and S_2. At intermediate temperatures, another isothermal type may, however, occur. The salt hydrate, stable in the binary system W–S_1 at the temperature considered, may suffer dehydration when the concentration of the second salt in the ternary system has

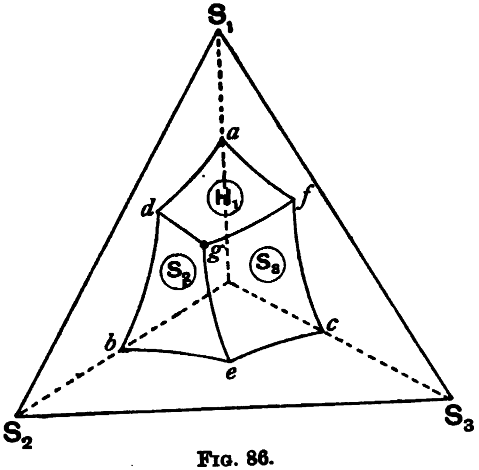


FIG. 86.

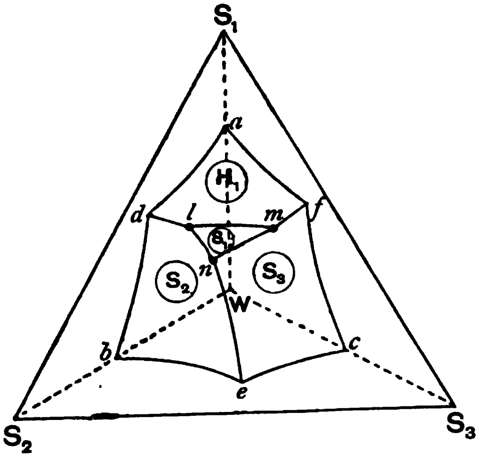


FIG. 88.

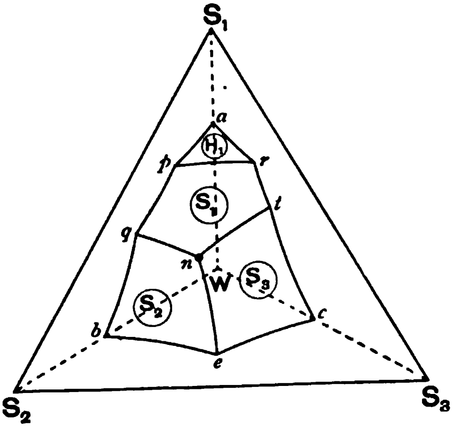
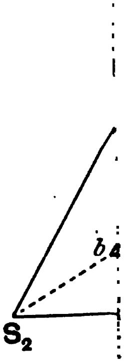
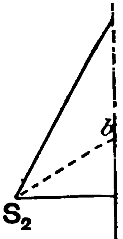
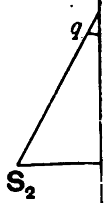


FIG. 92.







SHEET XI.

reached a certain value. The isotherm will then contain the saturation curves of H_1, S_1, and S_2, following each other in order (*cf.* § 44).

In the quaternary system W–S_1–S_2–S_3, where the salt hydrate H_1 appears as a solid phase, the isotherm (in plane projection upon the base of the tetrahedron) will show the simple type of Fig. 86 at a temperature sufficiently low. The anhydrous salt S_1 will be unable to exist as a stable solid phase. The isotherm will then contain only three saturation surfaces, those of H_1, S_2, and S_3; three saturation curves, being the intersections by pairs of these surfaces; and one isothermal invariant point, being the common point of intersection of the three curves and the three surfaces.

At a temperature sufficiently high, the quaternary isotherm will again be of the simplest type, as shown in Fig. 87. The hydrate is now unable to exist, and Fig. 87 differs from Fig. 86 only in the substitution of the saturation surface of the anhydrous salt S_1 for that of the hydrate H_1. Between the temperatures for which Figs. 86 and 87 obtain, a number of isothermal types occur which show the saturation surfaces of both the hydrate H_1 and the anhydrous salt S_1. There exists, namely, between these two temperatures a quaternary system invariant point; it is the point at which all four solid phases H_1, S_1, S_2, and S_3 are in equilibrium with a quaternary solution. In order to deduce the intermediate isothermal types, we must know the phase reactions which are in equilibrium at this invariant point. These reactions will, however, depend upon the relation which exists between the composition of the hydrate and that of the invariant solution, as we have already seen to be the case in the binary and in the ternary invariant systems in which both the hydrate H_1 and the anhydrous salt S_1 occur as solid phases (*cf.* § 44).

At the binary invariant point in the system W–S_1, where the two solid phases H_1 and S_1 are in equilibrium with an invariant solution, we found (§ 18) that the equilibrium reactions might be represented by one of the following schemes:

$\mathrm{H}_1 + S_1 \rightleftarrows$ Solution . . . . 1.

or $\mathrm{H}_1 \rightleftarrows$ Solution $+ S_1$ . . . . 2.

In order to determine which of these schemes represents the equilibrium in a given case, we must decide which of the phase reactions represented by them is capable of maintaining the constant composition of the liquid phase in the given case. On the addition of heat to the invariant system H_1–S_1–Solution, the hydrate dissolves, and if, by so doing, it raises the concentration of water in the solution, then anhydrous salt must dissolve simultaneously in order to counteract this effect; the equilibrium reactions will then be represented by scheme 1. If, on the other hand, the hydrate, in dissolving, raises the concentration of the salt in the solution, then anhydrous S_1 must simultaneously be deposited in order to maintain the constant composition of the solution, and the equilibrium reactions will then be represented by the scheme 2; we have called the system invariant point in this latter case a transition point.

At the ternary invariant point in the system W–S_1–S_2, where the three solid phases H_1, S_1, and S_2 are all in equilibrium with an invariant solution, the equilibrium reactions may be represented by one of the following schemes:

$$\mathrm{H}_1 + S_1 + S_2 \rightleftarrows \text{Solution} \quad . \quad . \quad . \quad . \quad . \quad 3.$$

or $$\mathrm{H}_1 + S_2 \rightleftarrows \text{Solution} + S_1 \quad . \quad . \quad . \quad . \quad . \quad 4.$$

If the hydrate, in dissolving, lowers the concentration of the salt S_1 in proportion to that of the water in the solution, then the anhydrous salt must dissolve simultaneously in order to counteract this effect. The dissolution of the hydrate will, in any case, lower the concentration of the salt S_2 in proportion to that of the water, and this salt must, therefore, also dissolve in order to maintain the constant composition of the liquid phase; the equilibrium will then be represented by scheme 3. If, however, the hydrate, in dissolving, raises the concentration of the salt S_1 in proportion to that of water in the liquid phase, then clearly the composition of this phase can only be maintained constant by the simultaneous separation of anhydrous S_1; the equilibrium reactions will then be represented by scheme 4. In our discussion of the ternary system, we restricted our consideration to this case, to the case in which the salt hydrate possesses a ternary transition point (§ 44). If the binary invariant system H_1–S_1–Solution marks a transition point, then the ternary invariant system H_1–S_1–S_2–Solution will generally, though not necessarily, mark a transition point also.

At the quaternary invariant point in the system W–S_1–S_2–S_3, where the four solid phases H_1, S_1, S_2, and S_3 are all in equilibrium with an invariant solution, the equilibrium reactions may similarly be represented by one of the following schemes :

$H_1 + S_1 + S_2 + S_3 \rightleftharpoons$ Solution . . . . 5.

or $H_1 + S_2 + S_3 \rightleftharpoons$ Solution $+ S_1$ . . . 6.

We shall assume in the following discussion that the quaternary invariant equilibrium is represented by the scheme 6. The hydrate will then possess a quaternary transition point, and we shall assume further, what in practice will then generally be the case, that the hydrate also possesses a ternary transition point in each of the systems, W–S_1–S_2 and W–S_3–S_1, where it can appear as a solid phase, and a binary transition point in the system W–S_1. Between the temperature of the isotherm shown in Fig. 86, at which the anhydrous salt S_1 is capable of existence as a solid phase in the binary, ternary and quaternary systems, and that of the isotherm shown in Fig. 87, at which the hydrate H_1 is incapable of existence, the four following invariant equilibria must, therefore, occur :

$H_1 \rightleftharpoons$ Solution $+ S_1$, at the binary transition temperature T_1, in the system W–S_1.

$H_1 + S_3 \rightleftharpoons$ Solution $+ S_1$ at the ternary transition temperature T_2, in the system W–S_1–S_3.

$H_1 + S_2 \rightleftharpoons$ Solution $+ S_1$ at the ternary transition temperature T_3 in the system W–S_1–S_2.

$H_1 + S_2 + S_3 \rightleftharpoons$ Solution $+ S_1$ at the quaternary transition temperature T_4, in the system W–S_1–S_2–S_3.

At each of these transition temperatures the isotherm will show a transition form. We will first consider the equilibrium at the quaternary transition point of the hydrate. The withdrawal of heat from the invariant system in equilibrium at this point causes the following phase reaction to occur :

$$\text{Solution} + S_1 \rightarrow H_1 + S_2 + S_3.$$

The temperature will not alter until a phase has been consumed by this reaction. If the liquid phase is the first to disappear a solid phase complex will alone remain. If the solid phase S_1 is the first to disappear, the following monovariant system will remain:

$H_1 + S_2 + S_3$ + Solution . . . . . . 7.

At every temperature below the quaternary transition temperature there will exist, therefore, one isothermal invariant solution saturated with the three solids $H_1 + S_2 + S_3$. This solution is clearly represented by the point g in Fig. 86, and we see that the isothermal type depicted in this figure obtains at temperatures below the quaternary transition point.

If heat is added to the system in equilibrium at the quaternary transition point, the following phase reaction occurs:

$$H_1 + S_2 + S_3 \rightarrow \text{Solution} + S_1.$$

When one phase has been consumed by the reaction, the system will gain a degree of freedom, and at temperatures immediately above the quaternary transition temperature T_4 the three following monovariant systems can exist:

$S_1 + S_2 + S_3$ + Solution . . . . . . 8.
$S_1 + H_1 + S_3$ + Solution . . . . . . 9.
$S_1 + H_1 + S_2$ + Solution . . . . . . 10.

The isotherm at a temperature immediately above T_4 shows, therefore, three isothermal invariant points, and it is represented in plane projection by Fig. 88. In this figure, the point n represents the solution saturated with the three salts $S_1 + S_2 + S_3$, since it lies at the common point of intersection of the three corresponding saturation surfaces; it represents, in other words, the saturated solution, at the temperature of the isotherm, in the monovariant system 8. The points m and l represent, similarly, the solutions saturated with the salts $S_1 + H_1 + S_3$ and $S_1 + H_1 + S_2$ in the monovariant systems 9 and 10 respectively. We see, therefore, that if, starting from that of the isotherm shown in Fig. 86, the temperature is raised above the quaternary transition point of the hydrate, a new saturation surface (lmn) appears—that of the anhydrous salt S_1—and this surface intersects the other three in such a way as to cut off their common point of intersection. At the transition temperature itself, the isotherm can still be represented by Fig. 86, but in this case the point g will represent a solution saturated with the four solids $H_1 + S_1 + S_2 + S_3$, the saturation surface of S_1 being represented by the single point g itself; this point g at the temperature T_4 will be not only an isothermal invariant point, but also a quaternary system invariant point, and the saturation surface of S_1 will grow out from it when the temperature is raised, as Fig. 88 shows.

It is characteristic of the isothermal type shown in Fig. 88 that the saturation surface of S_1 lies wholly within the tetrahedron and does not extend to either of the faces. Dehydration of the hydrate H_1 occurs in the quaternary system, but not in either of the ternary systems; the system W–S_1–S_2, which is represented within the triangle WS_1S_2 (Fig. 88), shows only the ternary saturation curves *ad* and *bd*, of H_1 and S_2, the system W–S_3–S_1 only the ternary saturation curves *af* and *cf*, of H_1 and S_3.

The ternary invariant point *d* represents the solution in equilibrium with $H_1 + S_2$. The addition of increasing amounts of S_3 to this solution, which still remains saturated with the two solids H_1 and S_2, will cause the point representing the composition of the resulting quaternary solution to traverse the saturation curve *dl* of $H_1 + S_2$. When the composition of the solution is represented by the point *l*, dehydration of the hydrate begins. The dissolution of the salt S_3 is now accompanied by the abstraction of water from the hydrate H_1, and the consequent appearance of S_1 as a third solid phase; the composition of the solution remains constant at the value represented by the isothermal invariant point *l* as long as the three solid phases $H_1 + S_2 + S_1$ are present. The addition of a third salt to the ternary invariant solutions *e* and *f* will lead similarly to dehydration of the hydrate when the composition of the liquid has reached the values represented by the isothermal invariant points *n* and *m* respectively.

When the temperature is raised above the value corresponding with the isotherm in Fig. 88, the saturation surface *lmn* of the anhydrous salt S_1 will continue to grow until finally it touches one of the faces of the tetrahedron. We will suppose that this saturation surface reaches first the face WS_1S_2, and the isotherm will then be represented by Fig. 89. The quaternary invariant point *l* of Fig. 88 approaches, and at the temperature of the isotherm in Fig. 89 actually coincides with, the ternary invariant point *d*. The three solids $H_1 + S_1 + S_2$

are then in equilibrium with a solution in the ternary system W–S_1–S_2. The point *d* in this figure is, therefore, a ternary system invariant point, and the temperature must be the transition temperature T_3 of the hydrate in the ternary system W–S_1–S_2, since this is the only temperature at which the three solids H_1, S_1 and S_2 can exist in equilibrium with a ternary liquid, Fig. 89 represents the second isothermal transition form. If the temperature is raised above T_3, the saturation surface of S_1, growing larger, will extend into the face WS_1S_2 of the tetrahedron, and the isothermal type shown by Fig. 90 is obtained.

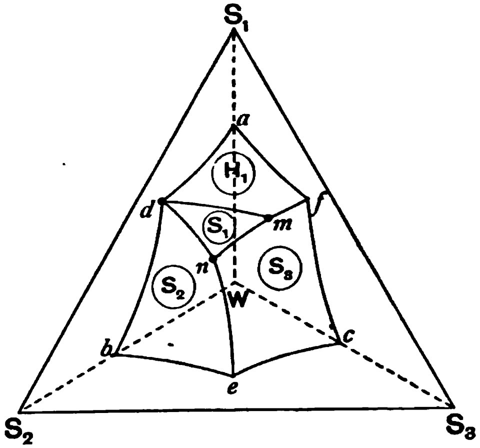


FIG. 89.

Dehydration of the hydrate now occurs in the ternary system W–S_1–S_2, and the quaternary invariant point *l* of Fig. 88 is replaced by the two ternary invariant points *p* and *q* of Fig. 90. We have already seen (§ 44) that at temperatures immediately above the ternary transition temperature T_3 of the hydrate the ternary isotherm must show three saturation curves; these are *ap* that of H_1, *pq* that of S_1, and *qb* that of S_2.

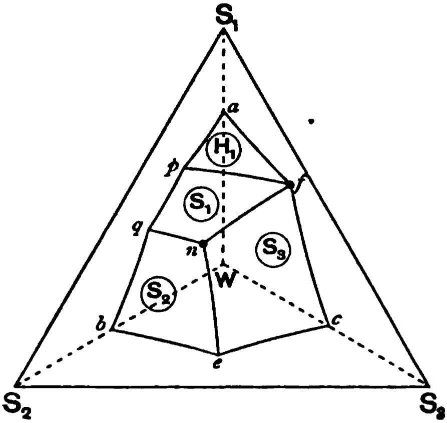


FIG. 91.

The isothermal invariant point *m* (Fig. 90) has approached the ternary invariant point *f* with the growth of the saturation surface of S_1, and when the temperature is still further raised it will ultimately coincide with this point. The three solids $H_1 + S_1 + S_3$ will then be in equilibrium with a ternary solution and the isotherm will be represented by Fig. 91. The point *f* in this figure is a ternary system invariant point, and the temperature must be the transition temperature T_2 of the hydrate in the ternary system W–S_1–S_3. Fig. 91 represents a third isothermal transition form. At a temperature slightly above T_2, the saturation surface of S_1 will extend into the face WS_1S_2, and the isothermal type will be given by Fig. 92. Dehydration of the hydrate occurs now in the ternary system W–S_1–S_3 also; since the temperature is immediately above the transition temperature of the hydrate in this system, this ternary isotherm also shows three saturation curves, *ar* that of H_1, *rt* that of S_1, and *tc* that of S_3. The quaternary invariant point *m* of Fig. 90 has been replaced by the two ternary invariant points *r* and *t*.

If we continue to raise the temperature, the saturation surface of S_1 will continue to grow at the expense of that of H_1 until, when the latter is completely displaced, the isotherm will show the simple type of Fig. 87, the existence of which at sufficiently high temperatures we have already deduced. The hydrate is here incapable of existing as a solid phase, and the isotherm shows only the three saturation surfaces of the anhydrous salts S_1, S_2 and S_3. The growth of the saturation surface of S_1 in Fig. 92 is accompanied by the gradual approach of the two ternary invariant points *p* and *r* to the binary saturation point *a*. These two ternary invariant points both represent solutions saturated with $H_1 + S_1$, and the saturation surface of H_1 will finally disappear when they reach coincidence with the point *a*. At the temperature at which this occurs the two solids H_1 and S_1 will be in equilibrium with a binary solution given by the point *a*, and the saturation surface of H_1 will be represented by this single point. The corresponding temperature—that at which H_1 and S_1 are both in equilibrium with a binary liquid—must be the transition temperature T_1, of the hydrate, in the binary system W–S_1, and above this temperature the isotherm will show the simple type of Fig. 87.

Summarising, we see that when a salt hydrate occurs as a solid phase in the quaternary system $W–S_1–S_2–S_3$, the isotherm shows the simple type of Fig. 86 at temperatures below the quaternary transition point of the hydrate, and the simple type of Fig. 87 at temperatures above its binary transition point. At temperatures between these two the isothermal types shown in Figs. 88, 90, and 92 can occur ; these types are separated from each other by transition forms, which occur at the ternary transition points of the hydrate in the two ternary systems $W–S_1–S_2$ and $W–S_1–S_3$ in which it can occur as a solid phase.

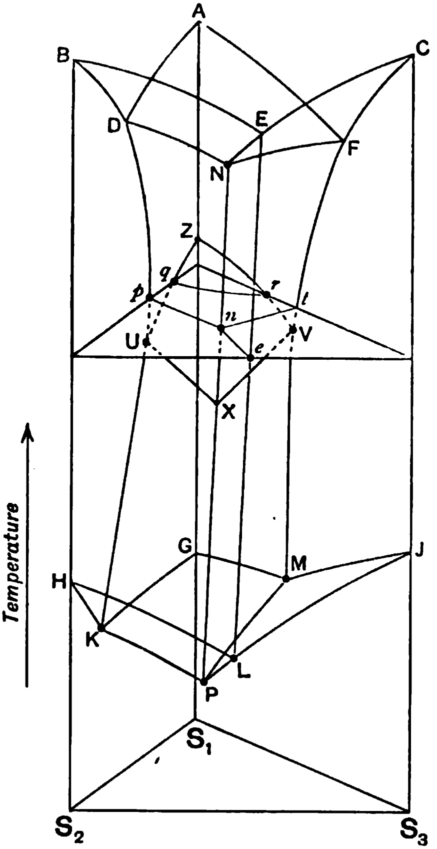


Fig. 93.

§ 59. By the aid of the foregoing considerations, the space figure which gives, by Jänecke's method, a partial representation of the polythermal conditions of equilibrium in the quaternary system can be constructed for the case in which a salt hydrate appears as a solid phase. It is given in Fig. 93, and this figure may be compared with Fig. 84, which represents, in a similar way, the polythermal conditions of equilibrium in the quaternary system where only the components appear as solid phases. The two ternary systems $W–S_1–S_2$ and $W–S_3–S_1$, in which the hydrate H_1 can exist as a solid phase, are represented on the side faces of the prism, and they may be compared with Fig. 53 of the previous chapter, which represents the typical ternary polytherm when a hydrate appears as a solid phase. The point Z is the transition point of the hydrate

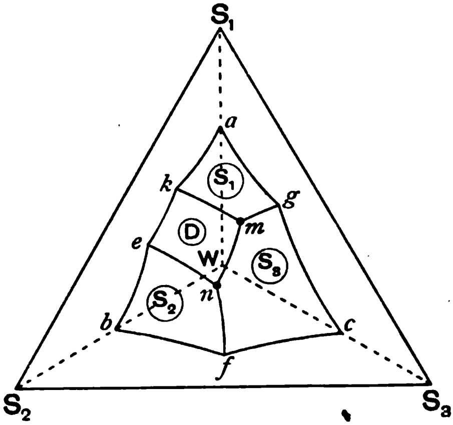
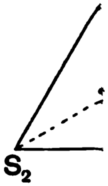


FIG. 95.



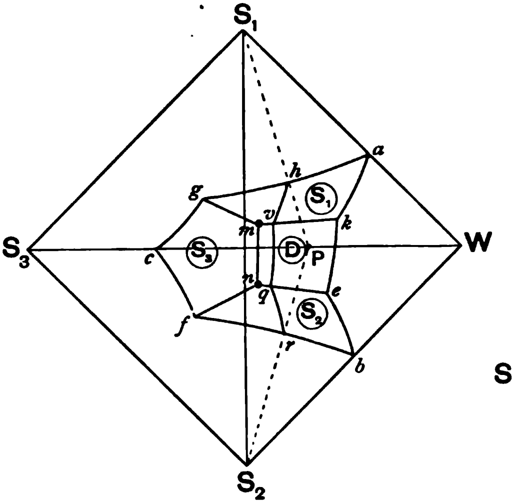
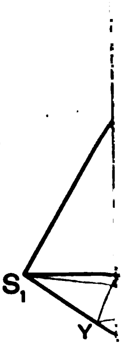


FIG. 97.



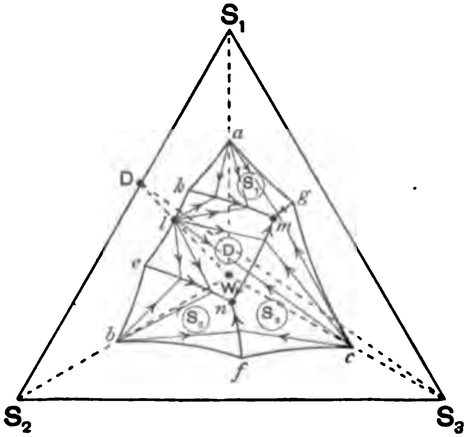
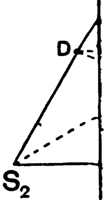


FIG. 99.



SHEET XII.

in the binary system W–S_1. The points U and V are ternary transition points of the hydrate in the systems W–S_1–S_2 and W–S_3–S_1 respectively. The system W–S_2–S_3 is still of the simplest type, and it is represented on the front face of the prism, whilst the system S_1–S_2–S_3 is completely represented by a space figure, as was the case in Fig. 84; the hydrate cannot appear in this anhydrous system and it is, therefore, also of the simplest type. We have already discussed in § 57 the relations existing at a quaternary eutectic point such as P in Fig. 93. This point differs from the corresponding point in Fig. 84 only in the fact that the four solid phases with which the invariant solution is in equilibrium are $H_1 + S_2 + S_3 +$ Ice; the anhydrous salt S_1, being incapable of existing at this temperature, is replaced by the hydrate H_1.

The quaternary transition point of the hydrate defines a second system invariant point X, where the four solid phases H_1, S_1, S_2, and S_3 are all in equilibrium with solution:

$$H_1 + S_2 + S_3 \rightleftarrows \text{Solution } X + S_1.$$

We have seen in the previous paragraph that four saturation curves radiate from this point, one in the direction of falling temperature which corresponds with the monovariant system 7 (§ 58):

$$H_1 + S_2 + S_3 + \text{Solution},$$

and three in the direction of rising temperature which correspond with the monovariant systems 8, 9 and 10:

$$S_1 + S_2 + S_3 + \text{Solution},$$
$$S_1 + H_1 + S_3 + \text{Solution},$$
$$S_1 + H_1 + S_2 + \text{Solution}.$$

The curve XP is the saturation curve of $H + S_2 + S_3$, and it ends in the quaternary eutectic point P where ice appears as a fourth solid phase. The curve XU is the saturation curve of $S_1 + H_1 + S_2$, and it ends in the ternary transition point U where these three solids are in invariant equilibrium with a solution in the ternary system W–S_1–S_2. The curve XV is the saturation curve of $S_1 + H_1 + S_3$, and it ends in the ternary transition point V where these three solids are in invariant equilibrium with a solution in the ternary system W–S_3–S_1. The curve XN is the saturation curve of $S_1 + S_2 + S_3$, and it ends in the ternary eutectic point N where these solids are in equilibrium with an anhydrous melt. The isothermal types in the neighbourhood of the quaternary transition point of the hydrate can be deduced as sections of this space figure. A section above both ternary transition points U and V and below the binary transition point Z is shown in Fig. 93, and reproduced in the plane of the paper in Fig. 94. It corresponds with Fig. 92 in our previous series of types, which represent perpendicular projections of the space isotherm upon the base of the tetrahedron.

The two figures (92 and 94) clearly depict the same isothermal type, represented, however, by two different methods. They differ only in the fact that the ternary saturation curves, which appear within the triangle $S_1S_2S_3$ in Fig. 92, have been projected into the sides of the triangle $S_1S_2S_3$ in Fig. 94; this is the characteristic difference between Jänecke's method of representation and the perpendicular projection, as we have already pointed out in § 56.

§ 60. We will next suppose that, besides the components, an anhydrous double salt can occur as a solid phase in the system W–S_1–S_2–S_3. We will suppose this double salt to contain the two simple salts S_1 and S_2, and we will denote it by D. The quaternary isotherm is then represented as a perpendicular projection upon the base of the tetrahedron in Fig. 95. The double salt must appear as a solid phase in the ternary system W–S_1–S_2 within a certain temperature range, namely, within its existence interval (§ 43). The ternary isotherm, within this range of temperature, will then show three saturation curves. The curves ak, ke, and eb of Fig. 95 are the ternary saturation curves of S_1, D, and S_2, respectively, in the system W–S_1–S_2. The addition of S_3 to the ternary invariant solution k saturated with S_1+D will cause the point representing the composition of the solution, which is supposed to remain saturated with these two salts, to traverse the curve km. This curve is the quaternary saturation curve of S_1+D, and it must end in a quaternary isothermal invariant point m, which represents a solution saturated, not only with S_1+D, but also with the third salt S_3. The invariant point m is the terminal point of two other quaternary saturation curves; these are gm, the saturation curve of S_1+S_3, which starts from the ternary invariant point *g*, and *mn* the saturation curve of $D + S_3$. In the same way, the point *e* represents the ternary solution saturated with *D* and S_2; *en* is the quaternary saturation curve of $D + S_2$, and it ends in a second quaternary invariant point *n*, which represents the solution saturated with $D + S_2 + S_3$. This point must form the terminal point of two other saturation curves, namely, *fn* that of $S_2 + S_3$, and *mn* that of $D + S_3$, the other terminal point of which is the quaternary invariant point *m*, as we have already seen. The three quaternary saturation curves *km*, *mn*, and *en*, and the ternary saturation curve *ke*, bound the quaternary saturation surface of the double salt *D*. It can be seen from Fig. 95 that the saturation surfaces of S_1 and S_2 are entirely separated by that of the double salt *D*. The two simple salts cannot therefore exist together in equilibrium with solution; they are then said to be incompatible. The saturation surfaces of *D* and S_3 meet, however, in the saturation curve *mn*, and these two salts can therefore exist together in equilibrium with solution; they are said to be compatible. We saw in § 41 that the double salt may be capable of existing as a solid phase in the ternary system, through the whole temperature range within which saturated solutions are possible. Its existence interval may extend from the temperatures of the eutectic points, where ice is present as a solid phase, to the melting point of the pure double salt. In this case, the two simple salts will be incapable of existing together at any temperature in equilibrium with ternary solutions. The ternary saturation curves *ak*, *ke*, and *eb* of S_1, *D*, and S_2, respectively, must always follow each other in order, and the quaternary saturation surfaces of S_1 and S_2 must, at all temperatures, be separated by that of *D*, as shown in Fig. 95.

We have seen, however, that the double salt may possess a transition point in the ternary system (§§ 39 and 40), and at the transition temperature, both simple salts and the double salt are in equilibrium with a ternary invariant solution. This transition point forms either an upper or a lower limit to the existence of the double salt as a solid phase in the ternary system.

In this case the existence of the double salt as a solid phase will be limited also in the quaternary system. If we assume that its existence is limited on the side of low temperatures, then, at a temperature sufficiently low, the double salt will be incapable of existing as a solid phase in the system, and the quaternary isotherm will show the simplest type—that depicted, for example, in Fig. 96, where the only saturation surfaces are those of the simple salts S_1, S_2, and S_3. We shall consider the way in which the change occurs from the type shown in Fig. 95 to that shown in Fig. 96. Between the temperatures of these two types, a quaternary invariant system occurs, namely, the system:

$$D + S_1 + S_2 + S_3 + \text{Solution},$$

formed by the double salt and all three simple salts in contact with an invariant solution. We may call the corresponding quaternary system invariant point the quaternary transition point of the double salt, in analogy to the ternary transition point of the double salt where the following invariant equilibrium exists:

$$D + S_1 + S_2 + \text{Solution}.$$

The phase reactions which occur when heat is added to, or removed from, the quaternary invariant system

$$D + S_1 + S_2 + S_3 + \text{Solution}$$

are very simply determined by the considerations which we applied to the ternary invariant system $D + S_1 + S_2 +$ Solution (§ 39). It is clear that if a phase reaction occurs in which some or all of the solid phases D, S_1, S_2, S_3 are either dissolved or deposited by the solution in any proportion, then the composition of the solution must alter, for since none of these solid phases contain water, the concentration of this component in the solution must be either decreased or increased by such a reaction. Since, however, the equilibrium reactions must be such as to leave the composition of the liquid phase unaltered, this phase can take no part in them. These phase reactions must be such as to involve the solid phases only, and they can, therefore, only consist in the formation of the solid double salt from the two solid simple salts, and its decomposition into these two:

$$S_1 + S_2 \rightleftarrows D.$$

The phase reactions which are in equilibrium in the quaternary invariant system $D + S_1 + S_2 + S_3 +$ Solution are, therefore, identically those which are in equilibrium in the ternary invariant system $D + S_1 + S_2 +$ Solution; in the former case, the third solid phase S_3 and the quaternary liquid, and in the latter case the ternary liquid, take no part in the reaction. The temperature at which the invariant equilibrium occurs must, therefore, be the same in the two cases, for the conditions of equilibrium cannot be affected by the presence of a solid phase, or the composition of a liquid phase, which plays no part in the equilibrium reactions, in the same way, for example, as they cannot be affected by the composition of the vessel which contains the equilibrium mixture. Although the equilibrium occurring at the transition point of the double salt is not affected by the composition of a solution which may be present, yet if that solution is a ternary one composed of water, S_1, and S_2, then there is only one such solution which is stable at the transition point, since the coexistence of three solid phases with solution defines, in this case, an invariant equilibrium. In the same way, if the solution in contact with S_1, S_2, and D at the transition temperature is a quaternary solution, and a fourth solid phase S_3 is present, then the equilibrium is invariant, but the temperature corresponding with it must be the same as that of the ternary invariant equilibrium. It is, namely, the temperature of the binary phase equilibrium,

$$S_1 + S_2 \rightleftarrows D.$$

which cannot be affected by the composition of a solution, or by the presence of an additional solid phase, which does not participate in the equilibrium reactions. We can, therefore, draw the important conclusion that the transition temperature of the anhydrous double salt in the ternary system W–S_1–S_2, *i.e.*, in the presence of a ternary liquid, is the same as that of the double salt in the quaternary system W–S_1–S_2–S_3, *i.e.* in the presence of a quaternary liquid. In the latter case, however, the presence of a third solid phase S_3 is necessary in order to render the conditions of equilibrium completely defined, the composition of the solution as well as the temperature.

The difference between the phenomena which occur at the transition point of the anhydrous double salt and those which occur at the transition point of the salt hydrate will be made clear by comparing the equilibria which occur at these points. The equilibria which occur at the transition point of the salt hydrate are

$H_1 \rightleftarrows$ Solution + S_1 in the binary system,
$H_1 + S_2 \rightleftarrows$ Solution + S_1 „ ternary „
$H_1 + S_2 + S_3 \rightleftarrows$ Solution + S_1 „ quaternary „

Here the solution participates in the equilibrium reactions, and its composition is therefore a defining factor for the transition temperature. The addition of a new component lowers the transition temperature of a salt hydrate in the same way that it lowers a melting point or a eutectic point. The equilibrium which occurs at the transition point of the anhydrous double salt is

$$S_1 + S_2 \rightleftarrows D,$$

where as many additional phases are present as is necessary to define all the conditions of equilibrium. These phases take no part, however, in the equilibrium reactions, and the transition temperature is therefore independent of the number of components in the system.

Let us now return to the quaternary isotherm which is represented in Fig. 95, and we will assume that the double salt the saturation surface of which appears in this isotherm possesses a transition point which forms a lower stability limit to its existence as a solid phase. If now the temperature is lowered, the ternary saturation curve *ke* of the double salt will diminish in length, the two points *k* and *e* will approach one another, and at the transition temperature *T* they will coincide in one point, which represents the ternary invariant solution saturated with $S_1 + S_2 + D$. We have shown that at the same temperature *T* the quaternary saturation surface of *D* must also disappear. The only way in which this can occur is by the gradual approach of the two quaternary saturation curves *km* and *en*, until, at the temperature *T*, they reach coincidence throughout their whole length. We will suppose that the quaternary isotherm at the transition temperature *T* is represented by Fig. 96; the ternary invariant points *k* and *e*, and the quaternary saturation curves *km* and *en* of Fig. 95, must be supposed to have just reached coincidence in the point *v* and the curve *vy* of Fig. 96. The ternary saturation curve of the double salt is represented in this figure by the single point *v*, its quaternary saturation surface by the single line *vy*. The point *v*, since it also lies on the ternary saturation curves of $S_1 + S_2$, represents the ternary system invariant solution saturated with the three salts $S_1 + S_2 + D$, and points on the line *vy*, since it also lies on the quaternary saturation surfaces of S_1 and S_2, represent a series of quaternary solutions saturated with $S_1 + S_2 + D$. The point *y* must, in this case, give the composition of the quaternary system invariant solution which is saturated with the four salts $S_1 + S_2 + D + S_3$. It is the transition point of the double salt in the quaternary system, and it occurs in the same isotherm (*i.e.*, at the same temperature) as the transition point *v* of the double salt, in the ternary system. When the temperature is altered, the ternary saturation curve of the double salt grows out from, or disappears in, the invariant point *v*, and its quaternary saturation surface grows out from, or disappears in, the saturation curve *vy*. This behaviour is distinct from that of the anhydrous salt S_1 when the hydrate H_1 can appear as a solid phase in the quaternary system; we saw in the previous paragraph that, in this case, the saturation surface of S_1 grew out from, and disappeared in, a quaternary system invariant point.

A quaternary solution in equilibrium with three solid phases forms a condensed monovariant system, and such a system is characterised, in general, by the property that it is in stable equilibrium over a range of temperature, but that to every definite temperature within that range there corresponds a definite composition of the liquid phase (§ 4). The monovariant system formed by the three solids S_1, S_2, and *D* in contact with a solution, in the quaternary system W–S_1–S_2–S_3, exists, however, as we have seen, only at the definite transition temperature *T*. It clearly cannot exist over a range of temperature, since below *T* the saturation surface of *D* does not exist, and above *T* the two simple salts S_1 and S_2 are incompatible, *i.e.*, can never be together in stable contact with a solution. This monovariant system can, therefore, exist at one temperature only, but to this temperature there corresponds, on the other hand, an infinite number of solutions of different composition which are in equilibrium with the three solids; they are the solutions represented by points on the curve *vy* of Fig. 96.

The curious behaviour of this monovariant system is due to the fact that the solution does not participate in the phase equilibrium,

$$S_1 + S_2 \rightleftarrows D.$$

The system can therefore only exist at the invariant temperature of this binary equilibrium, which in no way defines the composition of any quaternary liquid which may be present.

§ 61. The deduction which we have made concerning the transition point of the anhydrous double salt in the ternary and quaternary systems is a particular example of a more general law, the proof of which was given by Schreinemakers, and which was called by him " the principle of similar isothermal parts." This law, as applied to salt solutions, may be stated in the following way. If at a particular temperature in the system X–S_1–S_2, where X is a given solvent, the isothermal saturation curves of S_1 and of S_2 are interrupted by that of a binary compound of S_1 and S_2, then this will be the case, at the same temperature, where X is any other solvent; if the saturation curves of S_1 and of S_2 intersect without such interruption where X is a given solvent, then they will do so when X is any other solvent. The group of curves formed by the saturation curves of S_1, of S_2, and of all binary compounds of S_1 and S_2 which can exist, is called by Schreinemakers the isothermal part S_1S_2, and the principle is then enunciated in the following form: All ternary systems containing the components S_1 and S_2 possess similar isothermal parts S_1S_2. The rigid proof of this principle can only be given by thermodynamical methods, and its general validity shown only by a treatment which considers the metastable, as well as the stable, equilibria. We shall, therefore, not discuss it further than will suffice to show its application in the case of the transition point of the anhydrous double salt. For this purpose, we shall choose a projection of the quaternary isotherm which is clearer for our present purpose than the one which we have hitherto used. Fig. 97 represents the isotherm of Fig. 95 projected upon a plane parallel to the two opposite tetrahedral edges WS_3 and S_1S_2, instead of upon the base of the tetrahedron as in the latter figure; the lettering of the two figures corresponds, and a comparison will show that they represent the same isothermal type. We have already described the construction of this projection in § 54, and Fig. 97 may be compared with Fig. 78, which represents the simplest quaternary isothermal type in a similar projection. We may suppose the edge WS_3 of the tetrahedron (Fig. 97) to rest upon the ground plane and the edge S_1S_2 to be above this plane, though parallel to it, and perpendicular to WS_3, and we will consider sections of the tetrahedron through the upper edge S_1S_2. PS_1S_2 is such a section, where P is a point on the lower edge WS_3, representing a binary mixture of W and S_3. The points in the section PS_1S_2 represent mixtures which can be formed by bringing together the binary mixture P, of W and S_3, with the two salts S_1 and S_2. We shall assume that the section intersects only the saturation surfaces of S_1, D, and S_2, and such mixtures will then form either an unsaturated solution or a solution which is in equilibrium with one or two of the solid phases S_1, D, S_2; no phase complex will occur which contains the salt S_3 as a solid phase. It follows, therefore, that all saturated and unsaturated solutions which can be formed by mixing P, S_1, and S_2 will contain the two components W and S_3 in the same proportion as that in which they are contained by the binary mixture P; their compositions can, in other words, be expressed in terms of P, S_1, and S_2. The binary mixture P, and the two salts S_1 and S_2, can, in this case, be considered as the three components of a ternary system. The isotherm in this ternary system is given by the intersection of the section PS_1S_2 with the quaternary isotherm in Fig. 97. It shows the ternary saturation curves *hv*, *vq*, *qr*, of S_1, D, and S_2, respectively, and it can be compared with the ternary system W–S_1–S_2, which is represented on the face WS_1S_2 of the tetrahedron in Fig. 97, and which shows the ternary saturation curves *ak*, *ke*, and *eb* of S_1, D, and S_2. The only difference which exists between the two ternary systems W–S_1–S_2 and P–S_1–S_2, is that the solvent W in the former has been replaced by the solvent P in the latter. It is true that the solvent P is a binary mixture of W and S_3, and the solvent W is a chemical individual, but this does not affect the validity of the principle of similar isothermal parts. This principle states that if the system W–S_1–S_2 shows the saturation curves of S_1, D, and S_2 following each other in order, then this must also be the case in the system P–S_1–S_2 at the same temperature, where P is a certain binary mixture of W and S_3 represented by a point on the edge WS_3 (we premise, however, that the section PS_1S_2 does not intersect the saturation surface of S_3, *i.e.*, that the system P–S_1–S_2 is a true ternary system). This is true for every isotherm, and therefore for isotherms in the neighbourhood of the transition temperature of the double salt. All parts of the saturation surface of D must, therefore, disappear at one and the same temperature; immediately S_1 and S_2 become compatible in the ternary system W–S_1–S_2 they become everywhere compatible in the quaternary system W–S_1–S_2–S_3.

Hence we arrive at the conclusion which we have previously drawn, that the transition temperatures of the double salt in the ternary and the quaternary systems are identical, and that the quaternary saturation surface of the double salt disappears in a saturation curve, and not in an invariant point.

§ 62. Fig. 98 represents, within a regular tetrahedron, the complete quaternary isotherm in the case under consideration, where an anhydrous double salt D is formed. Its lettering corresponds with that of Figs. 95 and 97 which we have previously used, and which are projections of this complete space isotherm. An unsaturated solution is represented in Fig. 98 by a point in the space above the saturation surfaces. If water be evaporated from such a solution, the point representing its composition will move away from the point W, along a straight line passing through W, until it reaches one of the saturation surfaces. If, for example, this surface is the saturation surface of S_1, then on the further evaporation of water solid S_1 will separate, and the path representing the varying composition of the solution, as the evaporation of water is continued, will lie on this surface. We have already shown in § 55 how the paths of crystallisation on the saturation surface of S_1 can be determined, and we will briefly recall the reasoning given in that paragraph. During the separation of solid S_1 from the quaternary solution, the proportion of S_2 to S_3 contained by the solution must remain constant, and the behaviour will be that of a ternary system the components of which are W, S_1 and a certain binary mixture of S_2 and S_3, represented by a point such as T on the edge S_2S_3 of the tetrahedron. The path of crystallisation on the saturation surface of S_1 is therefore given by the intersection of the plane WS_1T with that surface. Since T may be situated anywhere on the edge S_2S_3, the paths of crystallisation are represented by curves on the quaternary saturation surface of S_1, radiating from the point A, and terminating on one of the quaternary saturation curves KM or GM. They are represented in this way in the plane projection given in Fig. 99. Similarly, the paths of crystallisation on the saturation surface of S_2 are represented, in this figure, by lines radiating from the point b, and those on the saturation surface of S_3 by lines radiating from the point c. Let us now consider an unsaturated solution such as that represented by P in Fig. 98. On the removal of water from this solution the point representing its composition will move along the straight line WPR until its position is given by the point Q on the saturation surface of the double salt. Here, separation of that salt will commence, and the subsequent path of crystallisation must lie on the saturation surface. The position of this path may be determined by the following considerations. The double salt itself is a binary compound of the two simple salts S_1 and S_2, and its composition is represented, therefore, by a point D, which lies on the edge S_1S_2 of the tetrahedron in Fig. 98. The composition of the salt mixture contained in the solution P is defined by the position of the point R in which the straight line WPR intersects the base of the tetrahedron. Now the composition of this salt mixture can be expressed in two ways, for the position of the point R may be referred to the triangle $S_1S_2S_3$ in the usual way, or it may be referred to the triangle DS_2S_3. In the latter case, the composition of the salt mixture will be given in terms of the double salt and the two simple salts S_2 and S_3. If the composition is expressed in this way, then the relative proportion of S_2 to S_3 contained in the salt mixture R, and therefore also in the unsaturated solution P, is given by the point T where the line DR cuts the edge S_2S_3. Further, the separation of the double salt from the solution will not affect this proportion, and during this stage of the evaporation the behaviour must be that of a ternary system the components of which are W, D, and the binary mixture T. The path of crystallisation on the saturation surface of D will therefore be given by its intersection with the plane WDT. This will clearly be a curve which radiates from the point *L*, in which the line *WD* (in the face WS_1S_2) cuts the ternary saturation curve *KE* of the double salt.

An unsaturated solution such as *U* (Fig. 98) will also deposit first the double salt on concentration, namely, when its composition is given by the point *V* on the saturation surface of *D*. The composition of the salt mixture contained in the solution *U* is defined by the position of the point *X*, in which the straight line *WUX* cuts the base of the tetrahedron. By referring this point to the triangle DS_1S_3, the composition of the salt mixture can be expressed in terms of the double salt and the two simple salts S_1 and S_3. In this case the proportion of S_1 to S_3 contained by the salt mixture *X* and the solution *U* is given by the point *Y*, and it will not be altered by the separation of the double salt from the solution. The path of crystallisation during this stage of the evaporation will again be given by the intersection of the plane *WDY* with the saturation surface of *D*, *i.e.*, it will be a curve on the surface radiating from the point *L*.

According to the composition of the original unsaturated solution, the points *T* or *Y* may be situated anywhere on the edges S_2S_3 or S_3S_1, but the paths of crystallisation on the saturation surface of *D* will in all cases be given by curves radiating from the point *L*, and terminating on one of the quaternary saturation curves *EN*, *MN*, or *KM*. They are represented in this way in the plane projection given by Fig. 99. It can be seen in this figure that the paths of crystallisation on two adjacent saturation surfaces run together on the quaternary saturation curve which forms their line of intersection. The six quaternary saturation curves are therefore also paths of crystallisation, and these run together in two groups of three at the points *m* and *n*. Both isothermal invariant points are, therefore, final drying-up points.

We may now deduce a rule which is frequently of great use in constructing the quaternary paths of crystallisation. We have seen that these paths of crystallisation, on the saturation surface of S_1, diverge from the point *a* (Fig. 99). This point represents the binary solution which at this temperature is saturated with S_1; it represents the solution, containing only the salt S_1, which is saturated with this salt. In the same way, the paths of crystallisation on the saturation surface of S_3

diverge from the point *b*, which represents the solution saturated with S_2 and containing only this salt. We saw in § 29 that the point *l* (Fig. 99), in which the line *WD* intersects the ternary saturation curve *ke* of the double salt, represents a saturated solution in the binary system *W–D*. It is seen, therefore, that the paths of crystallisation on the quaternary saturation surface of the double salt also diverge from the point *l* which represents the solution saturated with *D* and containing only this salt (or, more strictly, containing the two simple salts S_1 and S_2 in the correct proportion to form the double salt, without leaving excess of either). Again, the quaternary saturation curve *fn* is the path of crystallisation of a solution depositing both salts S_2 and S_3, and it diverges from the ternary invariant point *f*, which represents a solution saturated with $S_2 + S_3$, and containing only these two salts. We can deduce, therefore, the following rule: The path of crystallisation of a solution which is in equilibrium with one or two salts diverges from the point representing the saturated solution containing only that salt or those salts. It will be seen that on the quaternary saturation curve *mn* the arrows at opposite ends of the curve point in opposite directions. The meaning of this can be clearly seen from Fig. 98. The section WS_3D of the tetrahedron cuts only the saturation surfaces of S_3 and *D*, and the saturation curve *MN* of $D + S_3$. The system $W–S_3–D$ is therefore a true ternary system, for since only S_3 and *D* occur as solid phases, the composition of a liquid in this system can always be expressed in terms of *W*, S_3, and *D*. The corresponding ternary saturation curves are given by the lines *CZ* and *LZ* of Fig. 98; and *Z*, the intersection of the plane with the curve *MN*, is a ternary invariant point representing the solution saturated with $S_3 + D$ in the system $W–S_3–D$. Between the two quaternary drying-up points *M* and *N* there is, therefore, a ternary drying-up point *Z*. We have seen that the paths of crystallisation of a quaternary solution in equilibrium with the two salts *D* and S_3 must diverge from the point which represents a solution saturated with the two salts, and containing only these, *i.e.*, it must diverge from the invariant point *Z* in the ternary system $W–S_3–D$.

Hence, on one side of the plane WS_3D, the path of crystallisation runs in the direction from *Z* to *M*, and on the other side, in the opposite direction from Z to N, whilst a solution of the composition Z dries at that constant composition. It can, in fact, be seen that the plane section WS_3D divides the tetrahedron of reference into two other tetrahedra, and that the portions of the quaternary isotherm lying in each of these can be considered as giving the conditions of equilibrium in two quaternary systems, each of which shows only one isothermal invariant point, and is, therefore, of the simple type shown in Fig. 72. Thus, the system W–S_1–S_3–D is represented inside the tetrahedron WS_1S_3D, and the quaternary isotherm in this system is bounded in the face WS_3D by the ternary saturation curves CZ and LZ; the isotherm shows only three saturation surfaces, those of S_1, S_3, and D, and one isothermal invariant point, M, which represents the solution saturated with $S_1 + S_3 + D$. The system W–S_2–S_3–D is similarly depicted within the other part of the tetrahedron of reference; the isotherm is also bounded in the face WS_3D by the ternary saturation curves CZ and LZ, and it shows the saturation surfaces of S_2, S_3, and D, and an isothermal invariant point N representing the solution saturated with these three salts.

§ 63. We saw in the previous chapter that the ternary system W–S_1–S_2, where a double salt D existed as a solid phase, could be considered as formed from two simpler systems W–S_1–D and W–S_2–D, which were then represented within the triangle the vertices of which denoted these components. This condition held, however, only so long as the two invariant solutions K and E (Fig. 98) were congruently saturated, *i.e.*, so long as their compositions could be expressed in positive terms of water and the two solids with which they were in equilibrium (§ 30). Thus, the composition of the solution K must be capable of expression in terms of W, S_1, and D, or, in other words, the point K must lie within the triangle WS_1D. The composition of the solution E must be capable of expression in terms of W, S_2, and D, or the point E must lie within the triangle WS_2D. Both these conditions are fulfilled when the line WD cuts the saturation curve KE of the double salt, *i.e.*, when the double salt is not decomposed by water.

Exactly analogous to these are the relations which obtain in the quaternary system W–S_1–S_2–S_3, where the binary double salt D exists as a solid phase. It can be considered as composed of the two simpler systems W–S_1–S_3–D and W–S_2–S_3–D, only so long as both quaternary invariant solutions M and N are congruently saturated, *i.e.*, so long as their compositions can be expressed in terms of water and the three solids with which they are in equilibrium. For this condition to hold the point M (Fig. 98) must lie within the tetrahedron WS_1S_3D, the point N within the tetrahedron WS_2S_3D, and this is only the case when the plane section WS_3D intersects the quaternary saturation curve MN of $S_3 + D$, as in Fig. 98, when, therefore, the system W–S_3–D is a true ternary system. It is readily seen that if the points M and N lie on the same side of the plane WS_3D, so that the latter does not intersect the curve MN, then it must cut another saturation surface besides those of S_3 and D; the system W–S_3–D is then no longer ternary, and the system W–S_1–S_2–S_3 can, therefore, no longer be considered as composed of two simpler quaternary systems. The case in which the double salt D is decomposed by water is depicted in plane projection in Fig. 100. The ternary invariant solution e is in equilibrium with $D + S_2$, but the point e does not lie within the triangle WDS_2. This solution is incongruently saturated, and the line WD does not intersect the saturation curve of the double salt. The quaternary solution n is in equilibrium with $S_2 + S_3 + D$ since it lies at the intersection of the corresponding saturation surfaces, but it is not situated within the tetrahedron WS_2S_3D. This solution is also incongruently saturated, and the plane section WS_3D does not intersect the saturation curve mn, of $S_3 + D$. The system W–S_3–D is, therefore, not a ternary system. The paths of crystallisation on the saturation surface of the double salt are given, as we have seen, by lines which radiate from the point representing the solution in equilibrium with the solid double salt in the system W–D. The double salt in the present case is, however, decomposed by water, and the system W–D does not actually behave as a binary system. If the saturation curve ke of the double salt (Fig. 100) is produced to meet the line WD in the point l, then this point would represent the solution saturated with the double salt and containing the two simple salts in the same proportion as does the double salt itself. Such a solution, if it can exist at all, is in a state of metastable equilibrium, the stable condition of a mixture of this composition being a phase complex. The paths of crystallisation on the saturation surface of the double salt are, however, still given by lines which, if they were prolonged, would be found to radiate from the point *l*, as indicated in Fig. 100.

We have previously seen (§ 30) that if water be evaporated from the ternary solution *e* in contact with the two solids S_2 and *D* with which it is in equilibrium, then *D* alone is deposited whilst S_2 is redissolved. The composition of the liquid remains constant only as long as it is in contact with solid S_2, but in the presence of sufficient liquid the whole of the solid S_2 is eventually dissolved, and the composition of the solution alters again in the direction of the value represented by the point *k*, following the saturation curve *ek*. This is characteristic of the incongruently saturated solution. The point *k* is the final drying-up point for all ternary solutions, if the solid phases are removed from contact with the liquid as fast as they separate, since, in this case, the solution *e* can never be in contact with solid S_2.

The behaviour is similar in the quaternary system. It will be seen from Fig. 100 that the paths of crystallisation on the saturation surfaces of S_2 and *D* do not run together on the saturation curve *en*, for the arrow-heads on the saturation surface of *D* are directed away from this curve. It follows, therefore, that solutions represented on this curve, although they are in equilibrium with $S_2 + D$, do not deposit both these salts on the evaporation of water; they deposit only the double salt *D*, and if solid S_2 is actually present it is redissolved. As long as excess of solid S_2 still remains, the point representing the composition of the solution will move along the curve *en*, which is, therefore, in this sense, a path of crystallisation. In the presence of sufficient solution, however, all the solid S_2 will eventually be consumed, and a path on the saturation surface of *D* will then be followed. The behaviour of a solution such as that represented by the point *P* on the saturation surface of S_2 is therefore the following.

On the evaporation of water, it will deposit solid S_2, and the point representing its composition will move along the path *bP* until it reaches the saturation curve *en*. If the evaporation of water be continued, the double salt will then separate, and at the same time the solid S_2, which was deposited during the first stage of the evaporation, will now start to redissolve. The point representing the composition of the solution will follow the path *en* until the solid S_2 has been completely consumed in this way. It will then leave the path *en* and follow one of the paths on the saturation surface of D, until, finally, either the saturation curve *km* or *mn* is reached, depending upon the position of the point P. The solution will, in either case, dry at the constant composition *m*, and the point *m* is the final drying-up point, as is shown by the fact that the arrow-heads on the saturation curves which intersect in this point are all directed towards it. The incongruent invariant point *n* is not a final drying-up point, for the arrow-heads on the saturation curves which intersect here are not all directed towards it, as the following considerations will show. The solution saturated with the two salts D and S_3 and containing only these salts can, in this case, only exist as a metastable phase, since the system W–D–S_3 is no longer a ternary system. The point representing the composition of this metastable solution would be obtained by prolonging the quaternary saturation curve *mn* of $D + S_3$ until it intersected the triangular section WDS_3. The arrow-heads on the crystallisation path *mn* must then be directed away from this point of intersection, and hence, also away from the isothermal invariant point *n*.

If the solids are removed from contact with the liquid as fast as they separate, then there can never be a halt at the saturation curve *en*; the point which represents the composition of the solution depositing solid S_2 will pass directly from a path on the saturation surface of S_2 to a path on the saturation surface of D, without following the curve *en*. In the same way, the point representing the composition of a solution depositing $S_2 + S_3$ will pass directly from the curve *fn* to the curve *nm* without halting at the point *n*, provided the solid phases are removed as fast as they separate.

§ 64. The quaternary isotherm which is characterised by the occurrence of the saturation surface of an anhydrous double salt is represented by Jänecke's method in Figs. 101 and 102 The first of these figures represents the case in which all ternary and quaternary invariant solutions are congruently saturated, and it is to be compared with Fig. 99, from which it differs only in the fact that the ternary saturation curves are here contained by the sides of the triangle. Fig. 102 represents the case in which one ternary invariant solution (*e*) and one quaternary invariant solution (n) are incongruently saturated; it is to be compared with Fig. 100.

These figures are in some respects clearer, and for practical purposes more useful, than the corresponding perpendicular projections. We have seen that the paths of crystallisation on the quaternary saturation surface of a salt radiate from the point which represents a solution in equilibrium with that salt, and containing it only. In the Jänecke representation, the composition of the salt mixture contained by saturated solutions is alone represented, and, therefore, a saturated solution containing one salt only is denoted by the point which represents that pure salt. Thus the point S_1 in Fig. 101 represents a saturated solution containing only pure S_1, and the paths of crystallisation on the saturation surface of S_1 radiate, therefore, from this point. In the same way, a saturated solution which contains only the double salt (or which contains the two simple salts S_1 and S_2 in the same proportion as does the double salt) is represented by the point D itself, and the paths of crystallisation on the saturation surface of D radiate from this point, as shown in Fig. 101. It is immaterial whether the solution which is in equilibrium with the double salt, and contains only this salt, is capable of stable existence, or whether it can exist only as a metastable phase; the solution will be represented, in either case, by the point D itself. Thus in Fig. 102 the point D lies on the boundary of the saturation surface of S_2, and a saturated solution which contains the two simple salts in the same proportion as does the double salt can, therefore, only exist in stable equilibrium with solid S_2. The point D can also represent, however, a metastable solution which is in equilibrium with the solid double salt, a solution which is, therefore, supersaturated with the simple salt S_2, but the paths of crystallisation on the saturation surface of D in Fig. 102 still radiate from the point D. We have already directed attention to the fact that the paths of crystallisation are correctly represented by straight lines in Jänecke's representation (§ 56).

The distinction between the congruently and the incongruently saturated quaternary solution can be seen very clearly from Figs. 101 and 102. This is due to the fact that the triangular section WS_2D of the tetrahedron in Fig. 98 is given by the straight line S_3D in Figs. 101 and 102. (These figures can be obtained by a perspective projection, through the vertex W, of the space isotherm, and it is clear that every point in the section WS_3D must project, in this way, into a point on the line S_3D.) In Fig. 101, the line S_3D intersects the saturation surfaces of S_3 and of D, and the saturation curve *mn* of S_3+D. The system W–S_3–D will show, therefore, the isothermal saturation curves of S_3 and of D, and the isothermal invariant point representing a solution saturated with S_3+D. This system is, in other words, a true ternary system. The point *n* in this figure gives the composition of the salt mixture contained in the quaternary invariant solution which is saturated with the three salts S_2+S_3+D. This point lies inside the triangle S_2S_3D, and the composition of the salt mixture can be expressed, therefore, in terms of the three salts with which the invariant solution is saturated; the invariant solution is, in other words congruently saturated. It can be seen very clearly that the isotherm of Fig. 101 is divided by the line S_3D into two parts, each of which can be com-

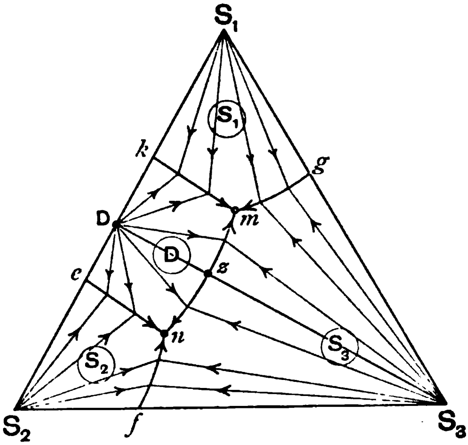


FIG. 101.

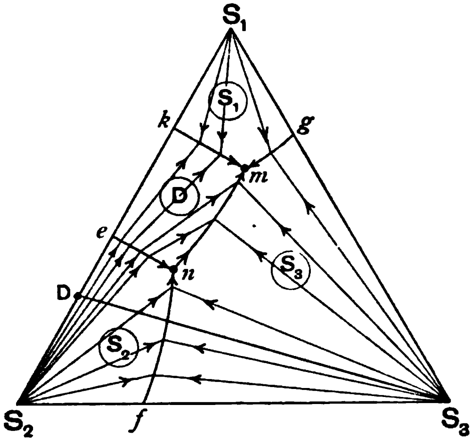


FIG. 102.

pared with Fig. 82, which represents the quaternary isotherm in a system of the simplest type.

In Fig. 102, the line S_3D intersects the saturation surfaces of S_3 and of S_2, and the saturation curve *fn* of $S_3 + S_2$. In the system W–S_3–D, the salt S_2 appears, therefore, as a solid phase, and since its composition cannot be expressed in terms of W, S_3, and D, the system is not a ternary system. The point n, again, represents the composition of the salt mixture contained in the quaternary invariant solution which is saturated with the three salts, $S_2 + S_3 + D$, but this point does not now lie inside the triangle S_2S_3D. The composition of the salt mixture can, therefore, no longer be expressed in terms of the salts with which the invariant solution is saturated; this solution is, in other words, incongruently saturated. It is clear that the isotherm of Fig. 102 is not divided into two simple isotherms by the line S_3D.

§ 65. Finally, we shall make brief mention of the case in which a ternary compound can appear as a solid phase in the quaternary system. The ternary compound may belong to either one of two types; it may be a hydrated double salt of the general formula $xS_1.yS_2.z\text{H}_2\text{O}$, *i.e.*, a compound of three components consisting of two simple salts and water, or it may be a triple salt of the general formula $xS_1.yS_2.zS_3$, *i.e.*, a compound of the three component salts.

If a hydrated double salt $xS_1.yS_2.z\text{H}_2\text{O}$ can occur as a solid phase, then within a certain temperature range its saturation curve must appear in the ternary system W–S_1–S_2, and its saturation surface must appear in the quaternary isotherm. We have not given a detailed discussion of the ternary system in which a ternary compound occurs as a solid phase, but we saw in the examples given in § 45 that the double salt hydrate may possess a ternary transition point which marks a temperature limit to its existence in the ternary system; it may, for example, break down at a certain temperature into two simple salt hydrates. In this case, the hydrated double salt will also possess a quaternary transition point which marks a temperature limit to its existence in equilibrium with quaternary solutions. We saw in § 60 that the transition temperature of the anhydrous double salt was the same in the quaternary as in the ternary system, and that, as a result of this, the saturation surface disappeared in a quaternary saturation curve at the transition temperature. This was due to the fact that the solid phases in equilibrium with the invariant solution at the transition temperature contained no water, and hence that the solution took no part in the equilibrium reactions. When the hydrated double salt occurs as a solid phase, it will no longer be true that the solid phases contain no water ; the equilibrium reactions may then involve the liquid phase, and the quaternary transition temperature may be lower than the transition temperature in the ternary system, exactly as was the case with the hydrated simple salt (§ 58). The saturation surface of the hydrated double salt will appear and disappear in a quaternary invariant point, and the isotherm in the neighbourhood of the transition temperature will be similar to that given in Fig. 88, the saturation surface of S_1 in that figure being replaced by that of the hydrated double salt. As the temperature moves further from the transition point, this saturation surface will grow, and eventually the isotherm will attain a transition form, similar to that shown in Fig. 89, at the ternary transition temperature of the hydrated double salt in the system W–S_1–S_2. Subsequently, the saturation surface will extend into the side face WS_1S_2, when the system W–S_1–S_2 will show the ternary saturation curve of the hydrated double salt ; the isotherm will be similar to that given in Fig. 90, the saturation surface of S_1 again being replaced by that of the hydrated double salt. This isothermal type will persist, for it is clear that the ternary compound $xS_1.yS_2.zH_2O$ cannot appear in either of the other ternary systems, and the saturation surface of the hydrated double salt cannot, therefore, extend into a second face of the tetrahedron, as was the case with that of the salt S_1 in the series of isothermal types given in § 58.

If a triple salt $xS_1.yS_2.zS_3$ can occur as a solid phase in the system, then the quaternary isotherm must contain the saturation surface of this salt. The only ternary system in which the triple salt can occur as a solid phase is the anhydrous system S_1–S_2–S_3, and since we are only considering the isothermal type at comparatively low temperatures (temperatures at which anhydrous salt mixtures are completely solid), the saturation surface of the triple salt will be confined to the space within the tetrahedron, and will not extend to either of the faces.

The triple salt T, like the double salt, may possess a transition point at which the three simple salts and the triple salt are in equilibrium with an invariant quaternary solution. Here, again, the solid phases in equilibrium with the invariant solution will contain no water, and the equilibrium reactions at the transition temperature must involve, therefore, only the solid phases. They will clearly be represented by one of the following schemes:

$$S_1 + S_2 + S_3 \rightleftarrows T$$

or

$$T \rightleftarrows S_1 + S_2 + S_3.$$

If the equilibrium is represented by the first of these schemes, the transition point will be a lower temperature limit to the existence of the triple salt as a solid phase; if it is represented by the second, the transition point will be an upper temperature limit. Assuming the former to be the case, then at temperatures below the transition point the only monovariant quaternary system which can exist is

$$S_1 + S_2 + S_3 + \text{Solution.}$$

The isotherm will be of the simplest type represented, for example, by Fig. 87, and will contain only one isothermal invariant point: that representing a solution saturated with the three simple salts $S_1 + S_2 + S_3$.

At temperatures above the transition point, the three following monovariant systems can exist:

$$S_1 + S_2 + T + \text{Solution,}$$
$$S_1 + S_3 + T + \text{Solution,}$$
$$S_2 + S_3 + T + \text{Solution.}$$

The isotherm will contain three isothermal invariant points p, q, and r (Fig. 103), each representing the saturated solution, at the temperature of the isotherm, in one of the above monovariant systems. The saturation surface of T intersects those of the three simple salts around the point which would be their common point of intersection if they were produced to meet. We have already shown that this saturation surface does not extend into either of the faces of the tetrahedron until temperatures are reached at which salt mixtures fuse.

§ 66. We will consider the system formed by water (W) and the two salts AB and CD, where A and C represent positive ions, B and D negative ions: these two salts contain no ion in common. The composition of a given aqueous solution of the salt *AB* can be expressed in terms of *AB* and *W*, that of a given aqueous solution of the salt *CD*, in terms of *CD* and *W*. Suppose, now, that the two given solutions are mixed. If they are sufficiently dilute, no precipitation of a solid phase will occur, for the resulting solution will be unsaturated, and its composition can clearly be expressed in terms of water and the two salts *AB* and *CD*. On the evaporation of water from this unsaturated solution, it may become saturated first with one of the salts *AB* or *CD*, and the continued evaporation will result, in this case, in the deposition of one of these. Here, again, it will be possible to express the compositions of the resulting saturated solutions in terms of *W*, *AB*, and *CD*, and the behaviour will clearly be that of a ternary system with these substances as components. We do not mean to assert that the solution contains the salts only in the form of the molecular individuals *AB* and *CD*, and we are not concerned with the state of homogeneous equilibrium existing within the liquid phase, as we have frequently emphasised. The results of a chemical analysis of the solution will, in general, be given in terms of the four ions *A*, *B*, *C*, and *D*. If in the system *W–AB–CD*, the only salts which occur as solid phases are *AB* and *CD*, the concentration of the ion *A* in the liquid phase will always be equivalent to that of the ion *B*, the concentration of the ion *C* will be equivalent to that of the ion *D*, and the composition of the solution will, therefore, always be capable of expression in terms of water and the two salts *AB* and *CD*.

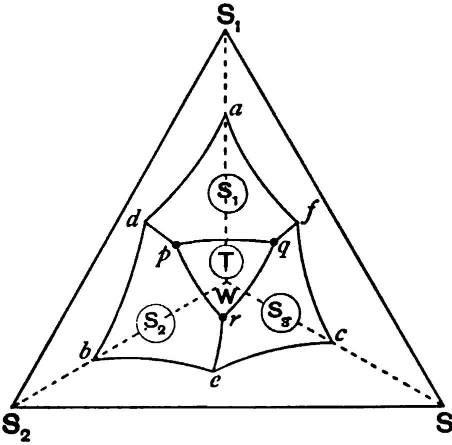


FIG. 103.

The following reaction may, however, take place in the system : $AB + CD \rightarrow AD + BC$, and this double decomposition may result in the separation of a new salt, let us say AD, in the solid phase. In this case, the concentration of the ion A remaining in solution will no longer be equivalent to that of the ion B, since some amount has been removed in the form of the solid salt AD, and, for a similar reason, the concentration of the ion C will no longer be equivalent to that of the ion D. The composition of the solution cannot be expressed in terms of water and the two salts AB and CD, and the system ceases to be ternary. We must determine the least number of substances which is necessary, in this case, to express completely the compositions of all phases. It may at first be supposed that the system is one of the five components W, AB, CD, AD, and BC, but the following considerations will show that this is not the minimum requisite number of components.

Let us suppose a solution to be formed by dissolving z moles of the salt AB and z moles of the salt CD in a given weight of water. Analytically, this solution will be identical with a solution formed by dissolving z moles of the salt AD and z moles of the salt BC in the same weight of water, since both solutions will contain z moles of each of the four ions A, B, C, and D. We will next suppose that a solution is formed by dissolving w moles of the salt AB, x moles of the salt CD, y moles of the salt AD, and z moles of the salt BC in m moles of water. The composition of the resulting solution can then be expressed, in molecular quantities, by the following form:

$$mW, wAB, xCD, yAD, zBC \quad . \quad . \quad . \quad . \quad . \quad . \quad 1.$$

Since, however, z moles of BC + z moles of AD can be equally well expressed as z moles of AB + z moles of CD, we can also represent the composition of the above solution by the form:

$$mW, (w+z)AB, (x+z)CD, (y-z)AD \quad . \quad . \quad . \quad 2.$$

We see that in virtue of the mathematical relationship:

$$1 \text{ Mole } AB + 1 \text{ Mole } CD = 1 \text{ Mole } AD + 1 \text{ Mole } BC,$$

we can express the composition of any phase in the system W–AB–CD–AD–BC in terms of water and three salts; the system is, therefore, one of four components, and not one of five. The composition of a given solution was expressed in terms of water and the four salts AB, CD, AD, and BC in form 1. In form 2, it was expressed in terms of water and the three salts *AB*, *CD*, and *AD*, but it is clear that we might have expressed this composition in terms of water and *any* three of the four salts. We may, for example, replace y moles of $AD + y$ moles of BC, in form 1 by y moles of $AB + y$ moles of CD, and the composition of the solution would then be given in the following form :

$$mW,(w + y)AB,(x + y)CD,(z - y)BC \quad . \quad . \quad . \quad 3.$$

The forms 2 and 3 both represent correctly the composition of a solution which was obtained by mixing water and four salts in the proportions given by the form 1. The number (z) of moles of the salt *BC* which were used in making this mixture may have been greater, or less, than the number (y) of moles of the salt *AD*. The concentration ($y - z$) of the salt *AD*, when the composition of the solution is given in the form 2, may, therefore, be either positive or negative, and if we fix the three salts *AB*, *CD*, and *AD* as independent components of the system *W–AB–CD–AD–BC*, we must be prepared for a graphical representation of negative concentration values. Similarly, if we fix the three salts *AB*, *CD*, and *BC* as independent components, and express the composition of solutions in the form 3, then we may expect negative values for the concentration ($z - y$) of the salt *BC*. It is clear, however, that either $y - z$ or $z - y$ must represent a positive number, and we can, therefore, express the compositions of *all* phases in the system in *positive* terms either of *W*, *AB*, *CD*, and *AD* (form 2) or of *W*, *AB*, *CD*, and *BC* (form 3).

The two salt pairs *AB*, *CD*, and *AD*, *BC*, which are formed from the four ions *A*, *B*, *C*, and *D* (the salts in either pair having no ion in common) are known as reciprocal salt pairs, and the system formed by the reciprocal pairs is conveniently represented by the notation $(\overset{+}{A},\overset{+}{C}) - (\overset{-}{B},\overset{-}{D})$. The system is characterised by the fact that a reciprocal reaction may occur between the salts. From what has been said, it follows that the system formed by the reciprocal salt pairs (without water) is a ternary system, and that formed by the aqueous solutions of the reciprocal salt pairs a quaternary system.

§ 67. We will consider the graphical representation of the ternary system formed by the reciprocal salt pairs $(\overset{+}{A},\overset{+}{C})$ —

$(\overset{-}{B},\overset{-}{D})$, without water. We may choose as components any three of the four possible salts; let us choose the salts *AB*, *CD*, and *AD*. The compositions of phases will be expressed in the form

$$pAB,qCD,(100-\overline{p+q})AD,$$

where the sum of the concentrations of the three components is equal to 100. We have hitherto used an equilateral triangle for the graphical representation of the ternary system when compositions are expressed in this form, but in the present case we shall use a right-angled isosceles triangle, for reasons which will become apparent later. The points *AB*, *CD*, and *AD* of Fig. 104 represent, then, the three pure components of the system $(\overset{+}{A},\overset{+}{C})-(\overset{-}{B},\overset{-}{D})$, as the corners of a right-angled isosceles triangle. Since the triangle is no longer equilateral, it is clearly not immaterial which side we choose to represent 100 per cent.; for this purpose we shall choose one of the shorter sides *AB*, *AD*, or *AD*, *CD*, these being the equal sides of the isosceles triangle. Through any point *R* within the triangle three lines *EF*, *GH*, *JK* are drawn, one parallel to each of the sides of the triangle. There are thus formed the three smaller isosceles triangles *RJG*, *RKF*, *RHE*, which have a common vertex in

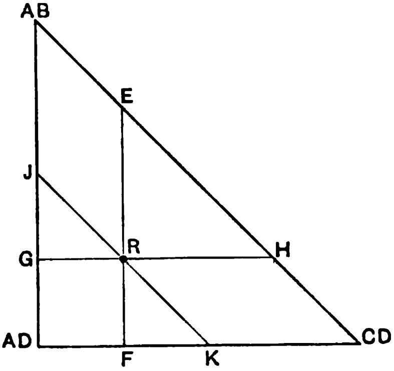


FIG. 104.

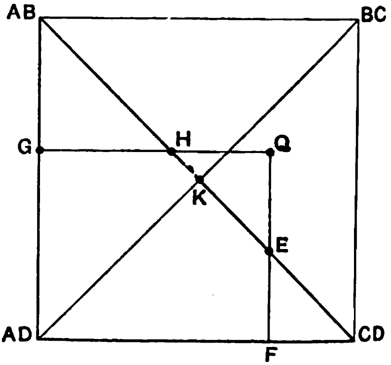


FIG. 105.

the point R. The sum of the shorter sides of these three isosceles triangles is

$$\begin{aligned} & GR + FK + RH \\ = {} & AD,F + FK + K,CD \\ = {} & AD,\ CD = 100 \text{ per cent.} \end{aligned}$$

We see that this sum equals the shorter side of the component triangle, and if the point R represents the composition of a phase in such a way that the length RF or FK gives the percentage p of the component AB, the length RG or GJ the percentage q of the component CD, contained by the phase, then the length RH or RE gives the percentage $100 - \overline{p + q}$ of the third component AD. We can therefore represent the composition of a phase containing the three components by a point within the triangle, and the percentage of any component is given by the distance of the point from the side opposite to the corner representing that component, not in a direction parallel to any one of the other sides, as when an equilateral triangle was used, but in a direction parallel to one of the shorter sides of the isosceles triangle.

We will now consider the meaning of a point such as Q (Fig. 105), which lies outside the component triangle AB, CD, AD. According to the method of representation which we have just described, this point denotes a phase containing QG parts of the component CD, and QF parts of the component AB, in a total of 100 parts, QG and QF being the distances of the point Q from the sides opposite the corners CD and AB respectively. The phase denoted by Q contains therefore

$$100 - \overline{QG + QF}$$

parts of the third component AD.

$$\begin{aligned} \text{Now } QG + QF &= F,AD + QE + EF \\ &= F,AD + QE + F,CD \\ &= AD,CD + QE \\ &= 100 + QE, \end{aligned}$$

$$\text{and, therefore, } 100 - \overline{QG + QF} = 100 - \overline{100 + QE} = -QE.$$

The point Q, which lies outside the component triangle, represents, therefore, a phase the composition of which can only be expressed in terms of the three salts *AB*, *CD*, and *AD* by assigning a negative value to the concentration of the latter. We see that the numerical value of this concentration is given, as before, by the distance *QE* (or *QH*), of the point *Q*, from the side opposite to *AD*, measured in a direction parallel to either of the shorter sides of the component triangle.

The fourth salt *BC*, which we have so far left unconsidered in the graphical representation, may be regarded as a phase the composition of which can be expressed in terms of the three components *AB*, *AD*, and *CD*, by using a negative value for the concentration of the component *AD*. We have seen that

$$100 \text{ Moles } AD + 100 \text{ Moles } BC = 100 \text{ Moles } AB + 100 \text{ Moles } CD,$$

and, therefore,

$$100 \text{ Moles } BC = 100 \text{ Moles } AB + 100 \text{ Moles } CD - 100 \text{ Moles } AD.$$

If the compositions of phases are expressed in molecular percentages, then the composition of 100 parts of the phase *BC*, given in terms of the three components, is the following:

$$100\,AB,\ 100\,CD,\ -100\,AD \quad . \quad . \quad . \quad . \quad 1.$$

Phases containing 100 parts of the component *AB* must be represented, in Fig. 105, by points on the line *AB*, *BC*, which is parallel to the side opposite to *AB*, and at a distance of 100 from it. Similarly, phases containing 100 parts of the component *CD* must be represented by points on the line *CD*, *BC*, and the point representing the salt *BC* itself, the composition of which is given by the expression 1, must lie, therefore, at the intersection *BC* of these two lines. The percentage of the third component *AD* in the phase represented by *BC* must be negative, since the point lies outside the triangle *AB*, *CD*, *AD*, and it is given numerically by either of the lengths *AB*, *BC*, or *CD*, *BC*, the distance of the point from the side *AB*, *CD*, opposite to *AD*, in a direction parallel to the shorter sides of the triangle. It is, therefore, equal to − 100, as required by the expression 1.

We see that if the points representing three of the salts are considered as three corners of a square, then the point representing the fourth salt is given by the fourth corner of the square. Phases the compositions of which can be expressed

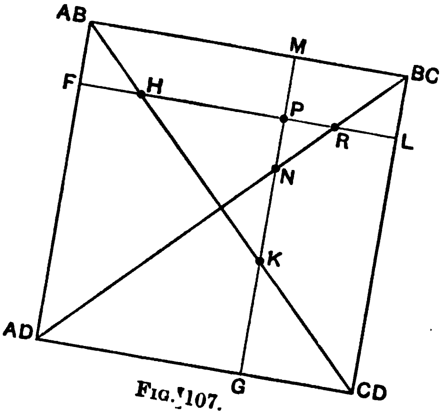


Fig. 107.

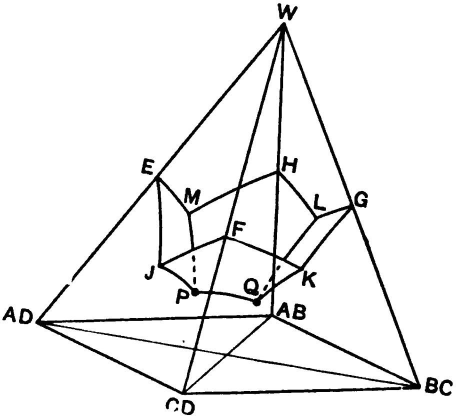


Fig. 110.

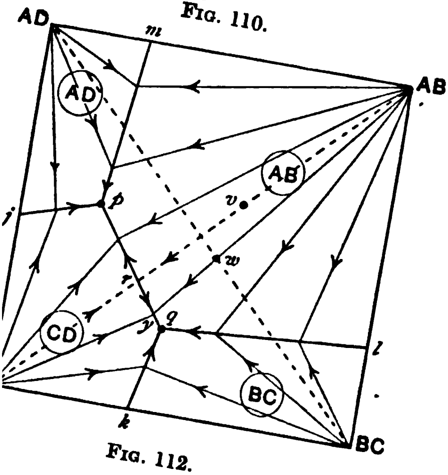
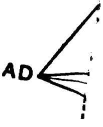
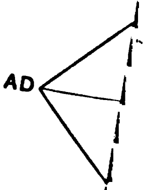
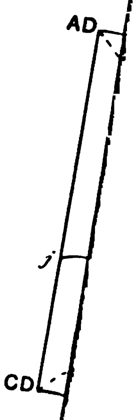


Fig. 112.







SHEET XIII.

in positive terms of the salts AB, CD, and AD are represented by points within the triangle AB, CD, AD, and phases the compositions of which can be expressed in positive terms of the salts AB, CD, and BC are represented by points within the triangle AB, CD, BC. We have already shown (§ 66) that the compositions of all phases in the system formed by the reciprocal salt pairs $(\overset{+}{A},\overset{+}{C})-(\overset{-}{B},\overset{-}{D})$ can be expressed in positive terms of one or other of these two salt triads, and they can, therefore, all be represented by points within the square AB, AD, CD, BC. It must be borne in mind that this is only true if the compositions of phases are expressed in molecular percentages, and it does not hold if gram-percentages are used. In order to make this clear, let us consider, as a concrete example, the reciprocal salt pairs $(\overset{+}{\mathrm{Na}}, \overset{+}{\mathrm{K}}) - (\overset{-}{\mathrm{Br}}, \overset{-}{\mathrm{Cl}})$. The salts of these reciprocal salt pairs are related by the equation

$$\mathrm{NaBr + KCl = NaCl + KBr.}$$

If we consider KBr as the "fourth salt," then its composition, expressed in molecular percentages of the other three, is :

$$100\mathrm{KBr} = 100\mathrm{NaBr},\ 100\mathrm{KCl},\ -100\mathrm{NaCl}.$$

Expressed in grams, it is the following

$$119\mathrm{KBr} = 103\mathrm{NaBr},\ 74{\cdot}5\mathrm{KCl},\ -\ 58{\cdot}5\mathrm{NaCl},$$

the numbers 119, 103, etc., being the gram-molecular weights of the various salts. The composition of the salt KBr referred to a total weight of 100 grams of this salt (*i.e.*, given in gram-percentages) is, therefore,

$$100\mathrm{KBr} = 86{\cdot}5\mathrm{NaBr},\ 62{\cdot}6\mathrm{KCl}, -49{\cdot}1\mathrm{NaCl}.$$

Now phases containing 86·5 per cent. NaBr are represented, in Fig. 106, by points on the line ML, the distance of this line from the side opposite to NaBr being 86·5 compared with the shorter side of the isosceles triangle, which measures 100. Similarly, phases containing 62·6 per cent. KCl are represented by points on the line NL, and the salt KBr is denoted, therefore, by the point of intersection L, of these two lines. The compositions of phases in the system formed by the reciprocal salt pairs, when they are expressed in gram-percentages, are represented by points which lie, not inside a square, but inside the quadrilateral L–NaBr–NaCl–KCl. Since there is no reason for choosing an unsymmetrical representation, compositions are always expressed, in practice, as molecular percentages. It is to be noticed that in reciprocal salt pairs such as $(\overset{+}{K_2},\overset{+}{Mg}) - (\overset{-}{SO_4},\overset{-}{Cl_2})$, where the relation which connects the four salts is

$$K_2SO_4 + MgCl_2 = 2KCl + MgSO_4,$$

the molecule of potassium chloride must be taken as K_2Cl_2, and the usual molecular weight must be doubled, for it is a necessary condition of the representation within a square, not only that the compositions of mixtures shall be expressed in molecular percentages, but also that the four salts shall be related by the equation

$$1 \text{ Mole } AB + 1 \text{ Mole } CD = 1 \text{ Mole } AD + 1 \text{ Mole } BC.$$

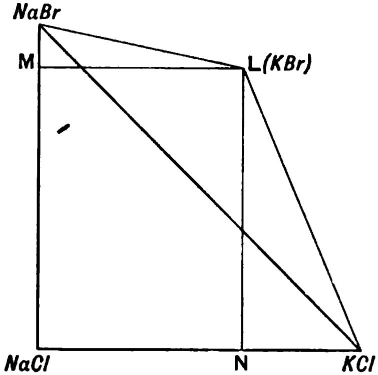


FIG. 106.

§ 68. We will suppose that the three salts which are to be considered as the components of the reciprocal salt pairs have not yet been defined. From the four salts, four different groups of three may be chosen, and either of these salt triads can be considered as components. This fact is expressed, by reference to the graphical representation, in the statement that the position of the point *P* (Fig. 107) can be referred to any one of the four triangles *AB*, *AD*, *CD*; *AB*, *BC*, *CD*; *AB*, *AD*, *BC*; or *CD*, *AD*, *BC*; and any one of these can be chosen as component triangle. We shall show that the point *P* represents a mixture of one definite composition, whichever triangle is considered as the component triangle, provided that the compositions of mixtures are represented by the method described in § 67.

Taking first the triangle *AB*, *AD*, *CD* as component triangle, we have the following expression for the composition of the mixture *P*:

$$PG \text{ Moles } AB,\ PF \text{ Moles } CD,\ -PK \text{ Moles } AD,$$

or, expressed in terms of the ions $\overset{+}{A}$, $\overset{-}{B}$, $\overset{+}{C}$, and $\overset{-}{D}$:

$(PG-PK)$ Moles $\overset{+}{A}$, PG Moles $\overset{-}{B}$, PF Moles $\overset{+}{C}$, $(PF-PK)$ Moles $\overset{-}{D}$.

It follows from the figure, however, that

$$PG-PK=KG=G,CD=PL,$$

and $$PF-PK=PF-PH=HF=F,AB=PM.$$

The composition of the mixture P, expressed in terms of the ions, is, therefore,

$$PL \text{ Moles } \overset{+}{A},\ PG \text{ Moles } \overset{-}{B},\ PF \text{ Moles } \overset{+}{C},\ PM \text{ Moles } \overset{-}{D}\ . \quad (1.)$$

We see that the sum of the concentrations of the two positive ions ($\overset{+}{A}$ and $\overset{+}{C}$) is

$$PL+PF=FL=AB,BC=100,$$

and the sum of the concentrations of the two negative ions ($\overset{-}{B}$ and $\overset{-}{D}$) is

$$PG+PM=MG=AB,AD=100.$$

The necessary condition that these two sums shall be equal is therefore fulfilled.

If we consider next the triangle AB, AD, BC as component triangle, the composition of the mixture represented by P is given by the expression:

$$PM \text{ Moles } AD,\ PF \text{ Moles } BC,\ PN \text{ Moles } AB,$$

or, in terms of the ions:

$(PM+PN)$ Moles $\overset{+}{A}$, $(PF+PN)$ Moles $\overset{-}{B}$, PF Moles $\overset{+}{C}$, PM Moles $\overset{-}{D}$.

Since, however,

$$PM+PN=MN=M,BC=PL,$$

and $$PF+PN=G,AD+PN=GN+PN=PG,$$

the composition is:

$$PL \text{ Moles } \overset{+}{A},\ PG \text{ Moles } \overset{-}{B},\ PF \text{ Moles } \overset{+}{C},\ PM \text{ Moles } \overset{-}{D},$$

and this is identical with the expression 1, of this paragraph, which we have already obtained for the composition of the mixture P, by referring it to the triangle AB, AD, CD. It can be shown in a similar way that the same expression is obtained when the composition of the mixture P is referred to either of the two remaining triangles. This method of graphical representation is, therefore, perfectly symmetrical with respect to all four salt triads, and this is the reason why, in § 67, we chose a right-angled isosceles triangle for the representation of the ternary system.

[If we had chosen the usual equilateral triangle, for example *AB*, *CD*, *AD* of Fig. 108, then by pursuing the argument used in § 67, we should have found that the fourth salt *BC* was represented by a point (*BC*) lying outside the triangle, and such that it formed the apex of a second equilateral triangle with *AB*, *CD* as base. If the composition of a given salt mixture *P* were expressed in terms of the three salts *AB*, *CD*, and *AD* the point *P* of Fig. 108 would be referred to the equilateral triangle *AB*, *CD*, *AD*; if the composition were expressed in terms of *CD*, *AD*, and *BC*, the point *P* would be referred, not to an equilateral, but to the obtuse angled isosceles triangle *CD*, *AD*, *BC*; the four salt triads would clearly not receive similar graphical representation.]

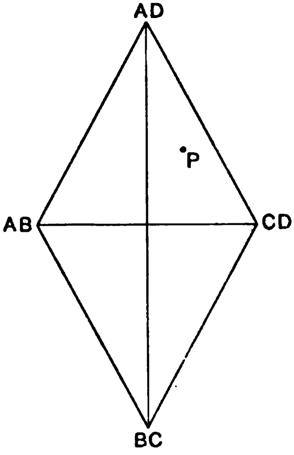


FIG. 108.

We have seen above that it is not necessary to express the composition of a mixture in the ternary system formed by the reciprocal salt pairs $(\overset{+}{A},\overset{+}{C})$ — $(\overset{-}{B},\overset{-}{D})$, in terms of any arbitrary salt triad, for the purpose of representing it by a point in a square. It is sufficient to express the composition in terms of the four ions, so that the sum of the concentrations of the positive ions, and therefore also of the negative ions, is equal to 100. If the composition of a phase *P*, expressed in this way, is

$$x \text{ Moles } \overset{+}{A}, (100-x) \text{ Moles } \overset{-}{C}, y \text{ Moles } \overset{+}{B}, (100-y) \text{ Moles } \overset{-}{D}. \quad (2.)$$

then by comparing this with the expression 1 of this paragraph

$$PL \text{ Moles } \overset{+}{A}, PF \text{ Moles } \overset{-}{C}, PG \text{ Moles } \overset{+}{B}, PM \text{ Moles } \overset{-}{D} \quad . \quad (1.)$$

we see that

$$\left.\begin{array}{r} x = PL \\ 100 - \ x = PF \end{array}\right\} PL + PF = AB, BC = 100.$$

$$\left.\begin{array}{r} y = PG \\ 100 - \ y = PM \end{array}\right\} PG + PM = AB, AD = 100.$$

The rule for determining the position of the point P, which represents a mixture of the composition given by the expression 2, is, therefore, the following. The square, the corners of which represent the four salts, and the side of which measures 100, being fixed, the point P is then chosen so that its distance PL from the side BC, CD (Fig. 107) measures x on the same scale, and its distance PG from the side AD, CD measures y. This rule may be easily remembered if it is noticed that the concentration x, of the ion $\overset{+}{A}$, is measured from the side BC, CD, which represents binary mixtures not containing the ion $\overset{+}{A}$; the concentration y, of the ion $\overset{-}{B}$, from the side AD, CD, which represents binary mixtures not containing the ion $\overset{-}{B}$. When the point is fixed in this way, its distances, PF and PM from the sides AB, AD and AB, BC, will measure $(100 - x)$ and $(100 - y)$, and they will give, therefore, the concentrations of the ions $\overset{+}{C}$ and $\overset{-}{D}$ respectively. It may be noticed here again that the concentration of a given ion is measured by the distance of the point from the side of the square which represents binary mixtures not containing that ion.

It must be clearly understood that no new theoretical considerations have been introduced in this and the previous paragraphs; these paragraphs deal only with the graphical representation of a ternary system of a particular type, namely, a system in which a reciprocal reaction (double decomposition) occurs. As components of the system, we have chosen three salts, for examples, AB, CD, and AD, and the "fourth salt" BC is to be considered as a ternary compound of these three, since its composition can be expressed in terms of them, although it is true that this involves the use of negative concentration values. Theoretically, however, there exists no difference between this case and the case in which a ternary compound of the general formula $AB.CD.AD$ can occur as a solid phase.

The formation of such a triple salt (T) is due to the occurrence of the following reaction in the system:

$$AB + CD + AD \rightarrow T\,(= AB.\,CD.\,AD) \quad . \quad . \quad 3.$$

The formation of the "fourth salt" (F) is due to the occurrence of the following reaction:

$$AB + CD - AD \rightarrow F\,(= BC) \quad . \quad . \quad . \quad . \quad 4.$$

or, as it is more generally written,

$$AB + CD \rightarrow AD + BC.$$

Equation 3 clearly shows that the composition of the triple salt T can be expressed in positive terms of the three remaining salts AB, CD, and AD; it is, therefore, the simplest method to choose these three as the components, and to consider the triple salt as a ternary compound. Equation 4 shows that the composition of the "fourth salt" (F) can only be expressed in terms of a negative quantity of the salt AD. Moreover, it is impossible to express the composition of any one of the four salts AB, CD, AD, and BC in positive terms of the other three, as we can see by transposing the symbols in equation 4, thus:

$$\begin{aligned} AB &= AD + BC - CD \\ CD &= AD + BC - AB \\ AD &= AB + CD - BC \\ BC &= AB + CD - AD. \end{aligned}$$

In this case there exists, therefore, no reason for choosing a particular salt triad as components, and for considering a particular salt as ternary compound. For this reason we have modified, in § 67, the usual graphical representation of the ternary system, in order to secure similar treatment for each of the four salts of the reciprocal salt pairs, and in this paragraph we have shown how, by expressing compositions in terms of the four ions, we can avoid specifying a particular salt triad as the component salts.

§ 69. We must next consider the graphical representation of the quaternary system $W\text{-}(\overset{+}{A}, \overset{+}{C})\text{-}(\overset{-}{B}, \overset{-}{D})$, which is formed by the reciprocal salt pairs and water. In order to represent the fourth component, water, a point must be chosen in space, and a symmetrical representation is obtained if this point is such that the space figure W, AB, AD, CD, BC (Fig. 109) forms a pyramid the side faces of which are equilateral triangles, and the base of which is the square *AB*, *AD*, *CD*, *BC*. Mixtures in the quaternary system will now be represented by points within the pyramid, and not, as in quaternary systems of the simplest type, by points within a regular tetrahedron. This change in the method of representing the quaternary system will involve consequences analogous to those which resulted from the representation of the ternary system within a square, instead of within an equilateral triangle. If we suppose, for example, that water and the three salts *AB*, *AD*, and *CD* have been chosen as the four components of the system, then all mixtures which can be formed from positive quantities of these four components will be represented by points within the tetrahedron *W*, *AB*, *AD*, *CD*, which forms half of the pyramid. This tetrahedron is, however, not regular, since its base *AB*, *AD*, *CD* is not an equilateral, but a right-angled isosceles triangle, and the edge *AB*, *CD* is, therefore, longer than the five remaining equal edges of the tetrahedron. A point within this tetrahedron represents the composition of a given quaternary mixture in such a way that the concentration of any component is measured by the distance of the point from the face opposite to that pure component in a direction parallel, not to any one of the edges, but to any one of the shorter and equal edges which are not contained by the face. The sum of the distances of the point from the four faces will equal the length of the shorter edge of the tetrahedron (*AD*, *CD* ; *AD*, *AB* ; *W*, *AB* ; *W*,*AD* ; or *W*,*CD*) ; it will be equal to the side of the square, which has been chosen to represent 100 per cent.[1]

In the ternary system $(\overset{+}{A}, \overset{+}{C})$–$(\overset{-}{B}, \overset{-}{D})$, where the three salts *AB*, *AD*, *CD* are chosen as components, a ternary compound—the fourth salt *BC*—occurs as a solid phase, and since its composition cannot be expressed in positive terms of the components, it is not possible to represent all mixtures in the system by points in the triangle *AB*, *AD*, *CD* (Fig. 109). We have seen, however, that those mixtures which could not be represented by points in the triangle *AB*, *AD*, *CD* could be represented by points in the triangle *AB*, *BC*, *CD*. The fourth salt *BC* must also occur as a solid phase in the quaternary system $W\text{-}(\overset{+}{A},\overset{+}{C})\text{-}(\overset{-}{B},\overset{-}{D})$ and it follows, therefore, that it is impossible to represent all mixtures in this system by points within the tetrahedron *W*, *AB*, *AD*, *CD*. Those mixtures which cannot be represented by points within this tetrahedron will, however, be represented by points in the tetrahedron *W*, *AB*, *BC*, *CD*, which forms the other half of the pyramid; thus it will be possible to represent *all* quaternary mixtures by points within the pyramid, just as it was possible to represent *all* ternary mixtures by points within the square.

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[1] A geometrical proof is not given, but the analogy with § 67 is so strict as to render such proof almost unnecessary.

§ 70. We have seen that the system formed by water and the reciprocal salt pairs is to be considered as a quaternary system in which a ternary compound occurs. The discussion of this case follows logically upon that given in § 65, of the case in which a triple salt *T* occurs as a solid phase in the quaternary system. We shall briefly recall the conclusions which we reached in that paragraph. At the invariant temperature at which the three simple salts S_1, S_2, and S_3, and the triple salt *T*, were in equilibrium with an invariant solution, the equilibrium reactions might be represented by the following scheme:

$$S_1 + S_2 + S_3 \rightleftarrows T \quad . \quad . \quad . \quad . \quad 1.$$

This temperature, the transition temperature of the triple salt, marked a limit to its existence as a solid phase in the system. If we assume, as usual, that the upper arrow of the equilibrium sign shows the reaction which occurs on the addition of heat to the invariant system, then the only monovariant system which can exist at temperatures below the transition point, in the case represented by the above scheme, is

$$S_1 + S_2 + S_3 + \text{Solution},$$

and the transition temperature is then the lowest at which the triple salt is capable of existing.

In the quaternary system $W\text{-}(\overset{+}{A},\overset{+}{C})\text{-}(\overset{-}{B},\overset{-}{D})$, the four solid salts *AB*, *CD*, *AD*, and *BC* (three components and one ternary compound) can only exist simultaneously in equilibrium with solution at a quaternary system invariant point. Since none of these solid phases contain water, the equilibrium reactions must be such as to involve only the solid phases; they are clearly represented by the scheme:

$$AB + CD \rightleftarrows AD + BC \quad . \quad . \quad . \quad . \quad . \quad 2.$$

At temperatures above the invariant temperature, the following monovariant systems will exist:

$$\left.\begin{array}{l} AB + AD + BC + \text{Solution} \\ CD + AD + BC + \text{Solution} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad 3.$$

At temperatures below the invariant temperature, the following monovariant systems will exist:

$$\left.\begin{array}{l} AD + AB + CD + \text{Solution} \\ BC + AB + CD + \text{Solution} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad 4.$$

According to our definition in § 17, this system invariant point is a transition point, for it does not mark a lower temperature limit to the existence of the liquid phase. An examination of the monovariant equilibria 3 and 4 will show, however, that the transition temperature does not mark a temperature limit to the existence of any one of the four salts, all four being capable of existence in equilibrium with other phases both below and above the transition temperature. It will be seen, however, that the monovariant systems 3, which are stable above the transition temperature, both contain the salt pair $AD + BC$ as solid phases; the monovariant systems 4, which are stable below the transition temperature, both contain the salt pair $AB + CD$ as solid phases. The transition point is a temperature limit, not to the existence of a particular salt, but to the coexistence of a salt pair, in equilibrium with solution. It marks the lowest temperature at which the two salts AD and BC, which do not possess a common ion, can both exist in equilibrium with quaternary solutions, and it marks the highest temperature at which the two salts AB and CD, which also possess no ion in common, can both exist in equilibrium with solutions.

The quaternary system in which a reaction occurs of the type shown by the equation 1 of this paragraph was characterised by the occurrence of a transition point which formed a temperature limit to the existence of one of the four salts in invariant equilibrium; it was the transition point of the triple salt T. The quaternary system in which a reaction occurs of the type shown by the equation 2 is characterised by the occurrence of a transition point which forms a temperature limit to the co-existence of a salt pair.

§ 71. We shall consider next the typical isotherms in the quaternary system $W\text{–}(\overset{+}{A},\overset{+}{C})\text{–}(\overset{-}{B},\overset{-}{D})$, and we will first suppose that the temperature is below the transition point of the reciprocal pairs. If the equilibrium reactions at this transition point are represented by the scheme 2 of the previous paragraph then the two following monovariant systems will be capable of stable existence:

$AD + AB + CD +$ Solution . . . . . 1.
$BC + AB + CD +$ Solution . . . . . 2.

and the temperature of the isotherm will be within the range of co-existence of the salt pair $AB + CD$.

The isotherm is represented in Fig. 110 by means of a pyramid, in the way we have described in § 69. As the basis of the quaternary system, we must consider the four ternary systems formed by water and two salts which have a common ion. These systems are $W\text{–}AB\text{–}AD$, $W\text{–}AD\text{–}CD$, $W\text{–}CD\text{–}BC$, and $W\text{–}BC\text{–}AB$, and the corresponding ternary isotherms are represented one in each of the triangular faces of the pyramid. We shall assume that the temperature of the isotherm is so far below the melting points of the pure salts that no saturation curves or surfaces can extend into the square base of the pyramid, *i.e.*, mixtures in the ternary system formed by the anhydrous reciprocal salt pairs are to be considered as completely solid.

The simple ternary system $W\text{–}AB\text{–}AD$ is represented, at the temperature of the isotherm, in the face W, AB, AD of the pyramid. It shows the two saturation curves HM and EM, of AB and AD respectively, and the ternary isothermal invariant point M, which represents the composition of the solution saturated with $AB+AD$. If a third salt—for example CD—is added to this ternary solution, the system becomes quaternary, and the alteration in the composition of the solution saturated with $AB + AD$, as increasing amounts of CD are added, is represented by points on the curve MP, which lies within the pyramid. When so much of the salt CD has been added that the composition of the solution is represented by the point *P*, the solution becomes saturated with this salt also, and a further addition of the salt effects no change in its composition. The point *P* is a quaternary isothermal invariant point, and it represents the composition of the solution which is saturated with the three salts *AD* + *AB* + *CD*. This is the solution saturated at the temperature of the isotherm in the monovariant system 1 of this paragraph.

The point *P*, since it represents the solution saturated with the three salts, must lie at the point of intersection of the saturation surfaces of *AD*, *AB*, and *CD*, and at the point of intersection of the saturation curves of *AD* + *AB*, *AD* + *CD*, and *AB* + *CD*. The first of these curves is the curve *MP*, which we have already considered. The saturation curve of *AD* + *CD* is given by *JP* in the figure, and it must start from the isothermal invariant point *J* in the ternary system *W–AD–CD*. The third curve which radiates from the point *P* is *PQ*, the saturation curve of the reciprocal pair *AB* + *CD*. Since the system *W–AB–CD* is not represented on a face of the pyramid, the saturation curve of *AB* + *CD* lies wholly within the space figure, and we shall consider its significance later.

The ternary system *W–AB–BC* is represented on the face *W*, *AB*, *BC* of the pyramid, and the point *L* represents the composition of the ternary solution which is saturated, at this temperature, with the two salts *AB* and *BC*. If to this solution increasing amounts of the third salt *CD* are added, the two salts *AB*, *BC* being still retained as solid phases, the composition of the solution will alter continuously, and the point which represents it will trace out the quaternary saturation curve, *LQ*, of *AB* + *BC*. When the composition of the solution is represented by the point *Q*, the solution has become saturated also with the third salt *CD*, and this point is, therefore, a second quaternary isothermal invariant point. It represents the composition of the solution saturated with the three salts *BC* + *AB* + *CD*, *i.e.*, the solution, saturated at the temperature of the isotherm, in the monovariant system 2. The point *Q* must lie at the point of intersection of the saturation surfaces of *BC*, *AB*, and *CD*, and at the point of intersection of the saturation curves of *BC* + *AB*, *BC* + *CD*, and *AB* + *CD*. The first of these is the curve *LQ*, which we have already considered. The saturation curve of *BC* + *CD* is given by *KQ* in the figure, and its terminal point is the point *K*, which represents the ternary solution saturated with both these salts. The curve *QP* is the saturation curve of *AB* + *CD*, and we have already seen that the other extremity of this curve is the quaternary invariant point *P*.

Summarising, we see that the isotherm of Fig. 110 contains four saturation surfaces.

Points on the surface *HMPQL* represent solutions saturated with *AB*,

Points on the surface *EMPJ* represent solutions saturated with *AD*,

Points on the surface *FJPQK* represent solutions saturated with *CD*,

Points on the surface *GKQL* represent solutions saturated with *BC*.

These saturation surfaces, intersecting in pairs, form five quaternary saturation curves.

Points on the curve *MP* represent solutions saturated with *AB* + *AD*,

Points on the curve *JP* represent solutions saturated with *AD* + *CD*,

Points on the curve *PQ* represent solutions saturated with *AB* + *CD*,

Points on the curve *LQ* represent solutions saturated with *AB* + *BC*,

Points on the curve *KQ* represent solutions saturated with *BC* + *CD*.

These saturation curves intersect in two groups of three, at the two quaternary invariant points.

The point *P* represents the solution saturated with

AD + *AB* + *CD*,

The point *Q* represents the solution saturated with

BC + *AB* + *CD*.

§ 72. For the further discussion of the system formed by solutions of the reciprocal salt pairs, we shall use the clearer representation which is afforded by a plane projection of the space figure. We may project the space figure of Fig. 110 upon the base of the pyramid by means of parallel lines perpendicular to the base, in the same way as we projected the simplest quaternary isotherm upon the base of the tetrahedron in § 53. The isothermal relations represented by means of a space figure in Fig. 110 are given in Fig. 111 as a perpendicular projection of this figure upon the base of the pyramid. The lettering of these two figures corresponds, and they can, therefore, be readily compared. The vertex *W* of the pyramid (Fig. 110) will project into a point perpendicularly below it, on the base of the pyramid. It is clear from the symmetry of the figure that this point must be the point of intersection *W* of the diagonals of the square in Fig. 111. The two pairs of opposite edges of the pyramid *W,AB*; *W,CD* and *W,AD*; *W,BC* (Fig. 110) will project into the diagonals *AB*, *CD* and *AD*, *BC* of the square in Fig. 111, whilst each triangular face of the pyramid will project into a quadrant of the square.

The four ternary systems which form the basis of a quaternary system are represented, therefore, one in each of the four quadrants of the square.

The quadrant *W*, *AB*, *AD* is, for example, the projection of the face *W*, *AB*, *AD* of the pyramid, and we find represented within it the isotherm in the ternary system *W–AB–AD*. The curve *hm* is the saturation curve of *AB* in this system, *em* is that of *AD*, and the point *m* represents the ternary invariant solution in equilibrium with $AB + AD$. Each of the four ternary invariant points *m*, *j*, *k*, and *l*, forms, as we have seen, the starting point of a quaternary saturation curve. Thus *mp* is the quaternary saturation curve of $AB + AD$, *jp* that of $AD + CD$, and these two curves intersect in the quaternary invariant point *p*, which represents the solution in equilibrium with the three salts $AD + AB + CD$ at the temperature of the isotherm. The point *q* represents, similarly, the quaternary invariant solution which is in equilibrium with the three salts $BC + AB + CD$. The various saturation surfaces, which are bounded by the saturation curves, are marked in Fig. 111 with the corresponding salts, and the significance of any particular saturation curve or point can, therefore, be readily seen. Thus the curve *pq* forms the boundary between the saturation surfaces of *AB* and *CD*, and it is, therefore, the saturation curve of the two salts $AB + CD$.

§ 73. If we project the space figure upon the base of the pyramid by means of lines which all radiate from the vertex *W*, instead of parallel lines which are perpendicular to the base, we shall obtain Jänecke's representation of the isotherm, as shown in Fig. 112. This figure differs from the perpendicular projection of Fig. 111 in the fact that the quaternary saturation curves alone appear within the square, the ternary saturation curves being contained by the sides of the square. We have already described Jänecke's representation of the simplest quaternary isotherm in detail in § 56, and the conclusions which we reached in that paragraph can be directly applied to the present case. We saw that this method of graphical representation gives, not the complete compositions of solutions, which can only be expressed by means of a figure in three dimensions, but the percentage compositions of the salt mixtures contained in saturated solutions. The actual construction of the diagram from experimental data is, therefore, very simple. It is only necessary to express the compositions of solutions in the following mathematical form :

$$mW, xAB, yCD, (100 - \overline{x + y})AD,$$

where the sum of the concentrations x, y, and $100 - \overline{x + y}$, of the three component salts, is equal to 100. The point in the square AB, AD, CD, BC which represents the ternary mixture :

$$xAB, yCD, (100 - \overline{x + y})AD$$

can be determined by the construction described in § 67, and it gives the position of the desired projection. As an alternative, the compositions of solutions may be expressed in terms of the four ions, by the following form :

$$mW, x\overset{+}{A}, (100 - x)\overset{+}{C}, y\overset{-}{B}, (100 - y)\overset{-}{D},$$

where the sum of the concentrations (always expressed as moles) of the positive ions, and therefore also of the negative ions, is equal to 100. The desired point is that which represents the ternary mixture :

$$x\overset{+}{A}, (100 - x)\overset{+}{C}, y\overset{-}{B}, (100 - y)\overset{-}{D},$$

as determined by the method described in § 68.

With the aid of Jänecke's representation, we will now consider the behaviour of certain salts of the reciprocal pairs when they are brought together with water. Saturated solutions the compositions of which can be expressed in terms of water and the two salts *AB* and *CD* are represented in Fig. 112 by points on the line *AB*, *CD*, since this figure gives only the compositions of the salt mixtures contained by saturated solutions. The line *AB*, *CD* traverses only the saturation surfaces of *AB* and *CD*, and intersects only the saturation curve *pq* of $AB + CD$. The only solid phases which appear in the systems *W–AB–CD* at the temperature of the isotherm, are, therefore, the two salts *AB* and *CD*. It follows from this that the system *W–AB–CD* is a true ternary system, since it will be possible to express the compositions of all phases in terms of the three components *W*, *AB*, *CD*; and the isotherm in this ternary system can be represented within an equilateral triangle by the method which we described in Chapter II for systems composed of water and two salts with a common ion. A study of the paths of crystallisation of solutions in the system *W–AB–CD* will also show that the behaviour is strictly that of a ternary system. We have shown in § 64 that the paths of crystallisation on the saturation surfaces are given in Jänecke's representation by straight lines radiating from the point which represents the pure salt, and they are constructed in this way in Fig. 112. The point *v* represents a solution the composition of which can be expressed in terms of water and the two salts *AB* and *CD*, and since it lies on the saturation surface of *AB*, the solution is just saturated with respect to this salt. If water is isothermally evaporated from the solution, solid *AB* will separate, and the point which represents in its successive positions, the compositions of the resulting solutions will traverse the path of crystallisation which passes through the point *v*. This path is, however, the diagonal *AB*, *CD* of the square, and the compositions of the resulting solutions will, therefore, also be capable of expression in terms of *W*, *AB*, and *CD*; in other words, they will be true ternary solutions. When the composition of the solution is represented by the point *r*, on the saturation curve of $AB + CD$, the solution itself will be just saturated with the second salt *CD*, and the continued evaporation of water will result in the simultaneous separation of both salts *AB* and *CD*, in the same proportion as that in which they are contained by the solution. The composition of the solution can now no longer alter, and the point r is, therefore, a ternary drying-up point; it is clearly the isothermal invariant point in the ternary system W–AB–CD.

It can be seen from Fig. 112 that the paths of crystallisation on the saturation surfaces of AB and CD run together on the saturation curve pq, which is, therefore, the path of crystallisation of a quaternary solution depositing the two salts AB and CD. We have shown in § 62 that the arrow-heads on a saturation curve which is a quaternary path of crystallisation for solutions depositing two salts are directed away from the point which represents a solution saturated with the two salts and containing them only. The arrow-heads on the saturation curve pq of $AB + CD$, must, therefore, be directed away from the ternary isothermal invariant point r; on one side of the diagonal AB, CD they are directed from r to p, and on the other side from r to q. This diagonal of the square does, in fact, divide the isotherm into two parts, each of which can be considered as the isotherm in a quaternary system of the simplest type. Thus the quaternary system W–AB–AD–CD is represented at this temperature within the triangle AB, AD, CD, and it shows only the three quaternary saturation curves jp, mp, rp, and the single quaternary invariant point p. It is, therefore, of the simplest type and can be directly compared with the simple system W–S_1–S_2–S_3 which is represented in Fig. 82; the isotherm in the latter system is depicted within an equilateral triangle, whilst the isotherm in the system W–AB–AD–CD is represented within a right-angled isosceles triangle in Fig. 112. The quaternary system W–AB–BC–CD is similarly represented in that figure, within the triangle AB, BC, CD, and it is also of the simplest type. We see here again a close similarity between the system formed by solutions of the reciprocal salt pairs and the quaternary systems, discussed in previous paragraphs, in which a binary or ternary compound occurs as a solid phase. We pointed out, for example, in § 64 that the isotherm in the system represented by Fig. 101 (where the saturation surface of a binary compound appears) is divided by the line S_3D into two parts which give the isothermal relations in two quaternary systems of the simplest type.

We will now consider the behaviour of the salt pair $AD + BC$. Solutions the compositions of which can be expressed in terms

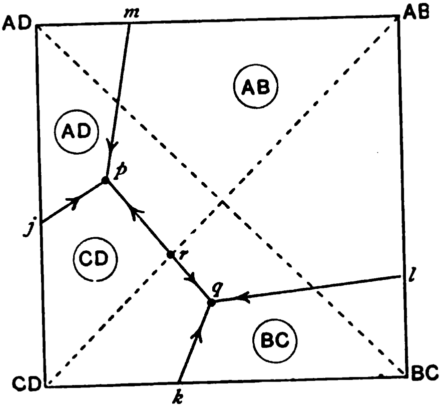

Fig. 114.

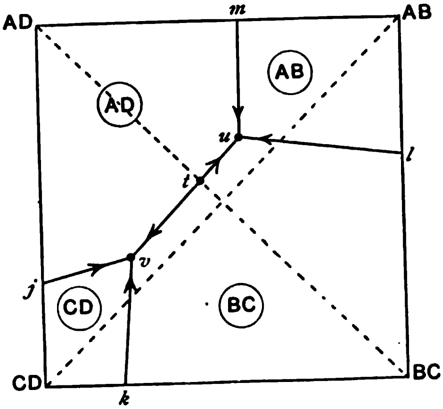

Fig. 115.

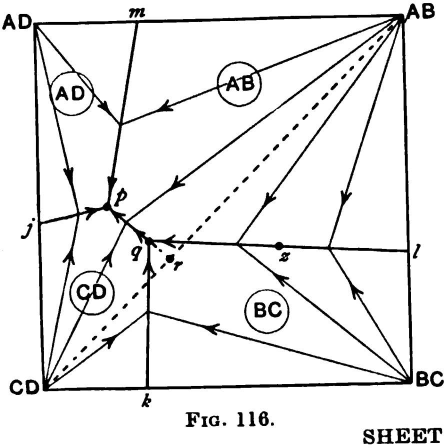

Fig. 116.

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of water and the two salts *AD* and *BC* are represented in Fig. 112 by points on the line *AD*, *BC*. This line traverses, not only the saturation surfaces of *AD* and *BC*, but also that of *AB*, and it follows, therefore, that solutions in the system *W–AD–BC* can be in equilibrium with the solid salt *AB*, the composition of which cannot be expressed in terms of the three substances *W*, *AD*, and *BC* alone. This system is not a ternary system, as can be seen very clearly from a study of the paths of crystallisation in the system. The point *w* in Fig. 112 represents a solution the composition of which can be expressed in terms of *W*, *AD*, and *BC*, and since the point lies on the saturation surface of *AB*, the solution is just saturated with this salt. On the evaporation of water, the solution will deposit solid *AB* and the point representing its composition will move along the path of crystallisation *AB*, *y*, which passes through *w*. The point will, in other words, move away from the line *AD*, *BC* and into the triangle *AD*, *CD*, *BC* ; it will be possible to express the composition of the resulting solutions in terms of water and the three salts *AD*, *CD*, *BC*, but not in terms of water and the two salts *AD*, *BC* alone. When the composition of the solution is represented by the point *y*, separation of the salt *CD* will begin, the path of crystallisation *rq* will be followed, and the solution will dry completely at the constant composition of the quaternary drying-up point *q*, with the simultaneous separation of the three salts *AB*, *CD*, and *BC*. It is clear that the system *W–AD–BC* is a quaternary system.

The temperature of the isotherm in Fig. 112 lies within the range of stable coexistence of the salt pair *AB*, *CD*. The saturation surfaces of *AB* and *CD* intersect in the saturation curve *pq*, the points of which all represent solutions which are in equilibrium with both solid *AB* and solid *CD*. The reciprocal salt pair *AB*, *CD* is said to be the stable pair at the temperature of the isotherm, and the two salts *AB* and *CD* which form this pair are said to be compatible. We have seen that the system formed by water and a stable reciprocal pair, like the system formed by water and two salts with a common ion, is a true ternary system.

The second reciprocal pair *AD*, *BC* is called the unstable pair and the two salts *AD* and *BC*, which form the unstable pair, are said to be incompatible. The saturation surfaces of *AD* and *BC* are entirely separated from each other by those of the stable pair, and no solution can exist, therefore, which is in stable equilibrium with both solid *AD* and solid *BC*. The system formed by water and an unstable reciprocal pair is a quaternary, and not a ternary, system.

§ 74. We have shown in § 70 that the quaternary system invariant point at which the four salts *AB*, *CD*, *AD*, and *BC* are all in equilibrium with a liquid phase is the transition point of the reciprocal salt pairs. The transition form of the isotherm at this temperature is shown in Fig. 113. All four saturation surfaces, and therefore all four saturation curves, meet in one point *s*, which is not only an isothermal, but also a system, invariant point, since the temperature of the isotherm is the invariant temperature of the transition point; it is the only temperature at which both reciprocal pairs *AB*, *CD* and *AD*, *CB* can exist in stable contact with a solution. At temperatures below the transition point, the stable salt pair *AB*; *CD* can alone exist in equilibrium with solutions. The isothermal type is then given by Fig. 114, where points on the saturation curve *pq* represent solutions in equilibrium with the stable pair *AB* + *CD*, the saturation surfaces of *AD* and *BC* being entirely separated. This is the type which we have discussed in the previous paragraphs and which has already been represented in Fig. 112.

At temperatures above that of the transition point, the salt pair *AD*, *BC* becomes the stable pair, and the two salts *AB*, *CD* which were compatible below the transition temperature, now become incompatible. The isothermal type is given by Fig. 115, in which points on the saturation curve *uv* represent solutions in equilibrium with the two salts *AD* + *BC*, the saturation surfaces of *AB* and *CD* being entirely separated from each other. It is clear from this isotherm that the system *W–AD–BC* is now a true ternary system, whilst the system *W–AB–CD* is quaternary. The isothermal invariant points in Figs. 114 and 115 represent solutions which are in equilibrium, at the temperature of the isotherm, with the stable salt pair plus one salt of the unstable pair. Thus the points *p* and *q* of Fig. 114, where the stable pair is *AB*, *CD*, represent solutions in equilibrium with (*AB*+*CD*)+*AD* and (*AB*+*CD*)+

BC respectively; these are solutions in the monovariant systems (4 of § 70) which exist at temperatures below the transition point. The points *u* and *v* of Fig. 115, where the stable pair is *AD*, *BC*, represent solutions in equilibrium with (*AD* + *BC*) + *AB* and (*AD* + *BC*) + *CD* respectively; they are solutions in the monovariant systems (3 of § 70) which exist at temperatures above that of the transition point.

If, starting from a temperature below the transition point, when the isothermal type is given by Fig. 114, the temperature is gradually raised, the saturation surfaces of *AD* and *BC* must continuously approach one another, until, finally, at the transition temperature, they meet in the system invariant point *s* as represented in Fig. 113; the two isothermal invariant points *p* and *q* will approach one another and ultimately coincide in the point *s*. It is clear, therefore, that at temperatures in the neighbourhood of the transition point, and before the two isothermal invariant points *p* and *q* have reached coincidence, these two points must both lie on one and the same side of the diagonal *AB*, *CD*, as represented in Fig. 116. If the temperature is raised above the transition temperature, the saturation surfaces of *AB* and *CD* must recede from each other, giving rise to the isothermal type of Fig. 115; but here again it is clear that, in the neighbourhood of the transition temperature, and as soon as the saturation surfaces of *AB* and *CD* have separated from each other, the two isothermal invariant points *u* and *v* of Fig. 115 must both lie on one and the same side of the diagonal *AD*, *BC*, as shown in Fig. 117. We will suppose that the isothermal relations in the system are represented by Fig. 116. The two salts *AB*, *CD* are then the stable reciprocal pair, since they can both exist in stable equilibrium with solutions represented by points on the saturation curve *pq*. This isotherm differs, however, from that represented in Fig. 114, where the two salts *AB*, *CD* also formed the stable reciprocal pair, in the fact that the diagonal *AB*, *CD* now intersects, not only the saturation surfaces of *AB* and *CD*, but also that of *BC*. Solutions the compositions of which can be expressed in terms of *W*, *AB*, and *CD* may, therefore, be in equilibrium with the solid salt *BC*, the composition of which cannot be so expressed. The system *W–AB–CD* is not a ternary system; in this case, the system formed by water and the stable pair, like that formed by water and the unstable pair, is quaternary. The isotherm represented in Fig. 116 is not divided by the line *AB*, *CD* into two simpler isotherms, and it can be seen that the saturation curve *pq*, of *AB* + *CD*, lies wholly within the triangle *AB*, *CD*, *AD*. The two solid salts *AB* and *CD* can, therefore, only exist in stable equilibrium with quaternary solutions which contain, besides these two, the salt *AD*; they cannot exist in stable equilibrium with quaternary solutions, represented by points in the triangle *AB*, *CD*, *BC*, which contain, besides them, the salt *BC*, nor can they exist in stable equilibrium with a solution which contains them only, and which would be represented by a point on the line *AB*, *CD*. A solution which contains only the salts *AB* and *CD*, and which is in equilibrium with these two solid salts, can only exist as a metastable phase, and it is represented, in Fig. 116, by the point *r*, in which the metastable prolongation of the saturation curve *pq* intersects the diagonal *AB*, *CD*. This point *r* corresponds with the ternary invariant point *r* in Fig. 114, but in the present case the point lies on the saturation surface of *BC*, and the *stable* solution *r* is, therefore, in equilibrium with solid *BC*, the *metastable* solution which is also represented by this point, and which is in equilibrium with *AB* + *CD*, being supersaturated with respect to the salt *BC*. The curve *pq* is the path of crystallisation of solutions depositing the two salts *AB* and *CD*, and the arrow-heads on this curve must, in accordance with the rule deduced in § 62, be directed away from the point *r*, which represents a (metastable) solution saturated with *AB* + *CD* and containing them only. The arrow-heads along the whole length of the curve *pq* must, therefore, be directed away from the point *q*, and towards the point *p*, and not, as in the case represented by Fig. 114, towards *q* on one side of the curve and towards *p* on the other.

It can now be seen that the quaternary invariant point *q* in Fig. 116 is not a final drying-up point, for the arrow-heads on the saturation curves which meet in this point do not all converge on it. If water is evaporated from the solution represented by the point *z*, for example, the two salts *AB* and *BC* will be deposited, and the point representing the composition of the solution will traverse the curve *lq* from *z* to *q*. When the composition of the solution is represented by the invariant point *q*, separation of the salt *CD* will begin, and the composition of the solution will remain constant as long as the three salts *AB*, *BC*, and *CD* are present. The evaporation of water from the solution *q* in contact with these salts will not, however, result in the simultaneous separation of further quantities of all three salts, for the arrow-heads on the saturation curve *qp* show that the point representing the composition of the solution can move away from *q* and along this curve. Points on the curve *qp* represent solutions in equilibrium with the two salts *AB* and *CD* alone, and the evaporation of water from the solution, when its composition is represented by the point *q*, must, therefore, cause the re-dissolving of the salt *BC*, which was deposited during the first stage of the evaporation. The composition of the solution will remain constant at the value represented by the point *q* only as long as the three salts are present, but the evaporation of water will cause the salt *BC* to re-dissolve; when it has been completely consumed, the system will regain a degree of freedom, and the point representing the composition of the solution will move from *q* to *p* along the saturation curve. The point *p* is a final drying-up point, for it can be seen that the arrow-heads on the saturation curves which meet in this point all converge on it; the solution will dry at the constant composition represented by this point, with the simultaneous separation of the three salts *AB*, *CD*, and *AD*. The point *q* is a drying-up point only if the solution reaches dryness before the whole of the salt *BC*, which is present as a solid phase, has been consumed. If the salts are removed from contact with the solution as fast as they separate, then the composition of the solution cannot even halt at the value represented by the point *q*, and much less can the solution dry at this composition; the point *p* is, in this case, the drying-up point of *all* quaternary solutions.

The difference between the behaviour of the two quaternary invariant solutions *p* and *q* (Fig. 116), when water is isothermally evaporated, is due to the fact that the solution *p* is congruently, the solution *q* incongruently, saturated. The solution *q* is in equilibrium with the three salts *AB*, *CD*, and *BC*, but since the point *q* does not lie within the triangle *AB*, *CD*, *BC*, the composition of this solution cannot be expressed in terms of water and the three salts with which it is in equilibrium; we have described such a solution (§§ 30 and 63) as an incongruently saturated solution. The solution p is in equilibrium with the three salts AB, CD, and AD, and since the point lies within the triangle AB, CD, AD, the composition of the solution can be expressed in terms of water and the three salts with which it is in equilibrium; the solution is congruently saturated.

When we say that the composition of the solution q cannot be expressed in terms of the three salts AB, CD, and BC, it is to be understood that we mean positive quantities of those salts, and when we said that the two solid salts AB and CD could not be in equilibrium with solutions which contained, besides them, the salt BC, we meant solutions which contained positive quantities of AB, CD, and BC. As a matter of fact, we have shown in § 67 that the composition of a solution represented by the point q, or by a point on the curve pq, can be expressed *mathematically* in terms of the three salts AB, CD, and BC, although such points lie outside the triangle AB, CD, BC; in order to do so, it is necessary, however, to admit a negative value for the concentration of the salt BC. If water is evaporated from the solution q in presence of the three salts AB, CD, and BC, its composition remains constant, and whatever may be the nature of the phase reactions which maintain this constant composition, it is clear that the composition of the salt mixture which is deposited must be mathematically identical with that of the salt mixture which remains in solution. The composition of the salt mixture which is deposited by the solution q on the evaporation of water cannot, therefore, be expressed in positive terms of the three salts AB, CD, and BC; it must be expressed in terms of a negative quantity of the salt BC. Since, however, the separation of a negative quantity of BC can only be explained physically by the dissolution of a positive quantity of that salt, we are led to the conclusion which we have already reached from a consideration of the paths of crystallisation; the solution q can, namely, only maintain its constant composition on the evaporation of water, by the dissolution of the solid salt BC, the presence of which is therefore essential to the maintenance of this constant composition. The behaviour of the incongruently saturated invariant solution in the system formed by water and the reciprocal salt pairs is exactly similar to that of the incongruently saturated solutions which may occur in the ternary or quaternary systems where a double salt can exist as a solid phase (§§ 30 and 63).

When the isothermal relations are those represented by Fig. 116, the stable salt pair *AB*, *CD* is said to be decomposed by water. The two salts can exist in equilibrium with one another, and with quaternary solutions represented by points on the curve *pq*, but they cannot exist, as we have already seen, in equilibrium with solutions which contain water and them only, solutions which are represented by points on the line *AB*, *CD*. The stable salt pair is then said to be in its transition interval. It is clear that the transition interval of the stable salt pair *AB*, *CD* is bounded on the side of high temperatures by the transition temperature, and, on the low side, by the temperature of that isotherm in which the quaternary invariant point *q* actually falls on the diagonal *AB*, *CD*; above the former temperature the salt pair *AB*, *CD* is not stable, and below the latter temperature it is not decomposed by water, for the isothermal type will then be given by Fig. 114, where both quaternary invariant solutions are congruently saturated, and the system *W–AB–CD* is a ternary system. By referring to § 43, the reader can convince himself of the strict analogy which exists between the transition interval of the stable salt pair in this quaternary system, and transition interval of the double salt in the ternary system.

The isothermal relations at temperatures immediately above the transition point are represented by Fig. 117. After the foregoing discussion it will not be necessary to consider these relations in detail. The two salts *AD*, *BC* form the stable reciprocal pair, but this pair is decomposed by water since the system *W–AD–BC* is not a ternary system; the temperature of the isotherm is, in other words, within the transition interval of the stable salt pair *AD*, *BC*. The quaternary invariant point *u* is incongruently saturated, and it is not a final drying-up point. The quaternary invariant point *v* is, on the other hand, congruently saturated, and it is the drying-up point of all quaternary solutions if the solid phases are removed from contact with the liquid phase as fast as they separate.

The transition interval of the stable pair *AD*, *BC* will extend from the transition temperature to the temperature of the isotherm in which the invariant point *u* actually falls on the diagonal *AD*, *BC*. Below the former temperature the salt pair *AD*, *BC* will not be stable, and above the latter it will not be decomposed by water, since the isothermal type will then be that shown in Fig. 115, where both quaternary invariant solutions are congruently saturated, and the system *W–AD–BC* is a ternary system.

§ 75. The polythermal relations in the quaternary system formed by solutions of the reciprocal salt pairs can be represented by Jänecke's method in the same way as was possible in the simple quaternary system (§ 57). These relations must, in the present case, be represented by a space figure within a square prism (Fig. 118), in place of the triangular prism which we used for the representation of the polythermal relations in the simple quaternary system (Fig. 84). A point within the prism represents a saturated solution in such a way that the distance of the point from the sides of the square horizontal section in which it lies gives the composition of the salt mixture contained by the solution, and the height of that section above the base of the figure gives the temperature of the solution; the water content of the solution finds no expression in the figure, and the representation is, therefore, incomplete, as must be any polythermal representation of the quaternary system (*cf.* § 57).

A system invariant point in the quaternary system

$$W\text{–}(\overset{+}{A}, \overset{+}{C})\text{–}(\overset{-}{B}, \overset{-}{D})$$

must represent a solution in equilibrium with four solid phases. As solid phases we may have the four salts *AB*, *CD*, *AD*, and *BC*; the invariant point is then the transition point of the reciprocal salt pairs, as we have already seen. As solid phases, we may also have three salts and ice, in equilibrium with an invariant solution, and it is clear that the three salts must consist of the stable salt pair at low temperatures, plus one salt of the unstable pair. Thus if we assume, as before, that the salt pair *AB*, *CD* is stable at low temperatures, then the two following invariant systems can exist:

$$\text{Ice} + AB + CD + AD + \text{Solution } X.$$
$$\text{Ice} + AB + CD + BC + \text{Solution } Y.$$

The two points X and Y, which represent these two invariant systems, are shown as eutectic points in Fig. 118. When the temperature is lowered below that represented by the point X, the solution solidifies completely to a complex of the four solid phases Ice, AB, CD, and AD. The phase reactions which are in equilibrium at this eutectic point, are therefore given by the following scheme:

$$\text{Ice} + AB + CD + AD \rightleftarrows \text{Solution } X,$$

and at temperatures above that of the point X the four following monovariant systems can exist:

Ice + AB + CD + Solution . . . . 1.
Ice + AB + AD + Solution . . . . 2.
Ice + CD + AD + Solution . . . . 3.
AB + CD + AD + Solution . . . . 4.

The phase reactions in equilibrium at the eutectic point Y are given, similarly, by the following scheme:

$$\text{Ice} + AB + CD + BC \rightleftarrows \text{Solution } Y,$$

and at temperatures above that of the point Y, the four following monovariant systems can exist:

Ice + AB + CD + Solution . . . . 5.
Ice + AB + BC + Solution . . . . 6.
Ice + CD + BC + Solution . . . . 7.
AB + CD + BC + Solution . . . . 8.

Eight corresponding polythermal saturation curves will diverge, therefore, from the two eutectic points in the direction of rising temperature. Of these eight curves the four which correspond with the monovariant systems 2, 3, 6, and 7 must clearly terminate, one in each face of the square prism, at the ternary eutectic points in the systems formed by water and two salts with a common ion; these are the four curves XF, XG, YE, and YH of Fig. 118. The monovariant systems 1 and 5 are identical, and the corresponding saturation curve—that of the stable salt pair plus ice—extends, therefore, continuously from one quaternary eutectic point to the other; it is the curve XY of Fig. 118. The two remaining saturation curves, corresponding with the monovariant systems 4 and 8, represent solutions in equilibrium with the two salt triads formed by the stable salt pair and one salt of the unstable pair; the curve XS is the saturation curve of $AB + CD + AD$, and the curve YS is that of $AB + CD + BC$. These two curves must intersect in the quaternary system invariant point at which all four salts are in equilibrium with an invariant solution. This is the point S of Fig. 118, and it is the transition point of the reciprocal salt pairs where, therefore, the following phase reactions are in equilibrium :

$$AB + CD \rightleftarrows AD + BC.$$

At temperatures below this point the following monovariant systems can exist :

$$AB + CD + AD + \text{Solution},$$
$$AB + CD + BC + \text{Solution},$$

and these are represented, as we have just seen, by the saturation curves SX and SY, which terminate in the quaternary eutectic points. At temperatures above the transition point the following monovariant systems can exist :

$$AD + BC + AB + \text{Solution},$$
$$AD + BC + CD + \text{Solution},$$

and these are represented by the two polythermal saturation curves SM and SN, which diverge from the point S in the direction of rising temperature. These two curves end in the ternary eutectic points M and N, which give the compositions of the anhydrous salt melts in equilibrium with the two salt triads, in the ternary system $(\overset{+}{A}, \overset{+}{C})$–$(\overset{-}{B}, \overset{-}{D})$.

Between the two saturation curves SM and SN there extends a polythermal saturation surface, which is shown by the shaded area in Fig. 118, and points on this surface represent solutions which are saturated with the two salts $AD + BC$, with which the solutions represented on the boundary curves are also saturated; it is the polythermal saturation surface of the stable reciprocal pair at these temperatures. The saturation surface of the salt pair $AB + CD$, which is stable below the transition point, is similarly shown by the shaded area between the saturation curves SX and SY.

Isotherms in the system represented by Fig. 118 are given by plane horizontal sections of the space figure ; some of these sections have been constructed. The intersections of a plane

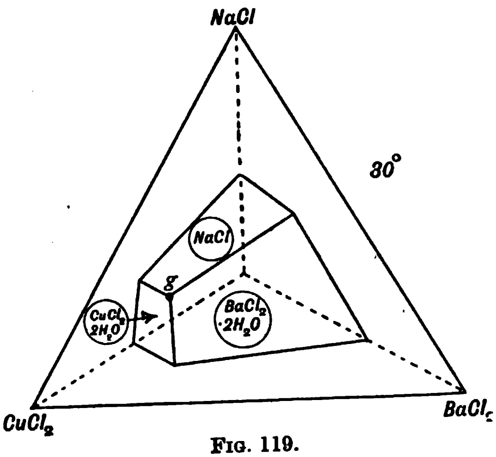


FIG. 119.

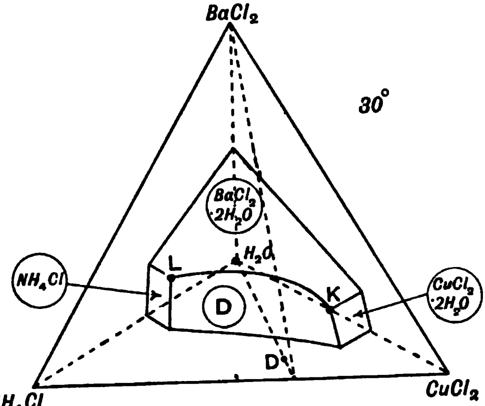


FIG. 121.

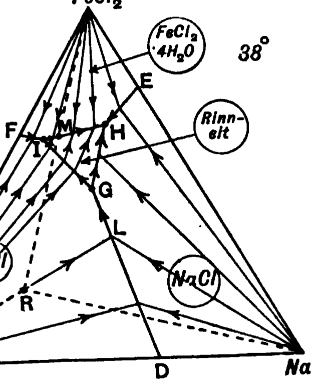
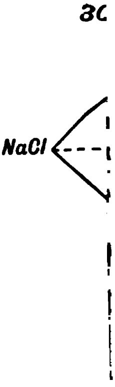
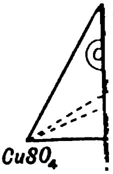
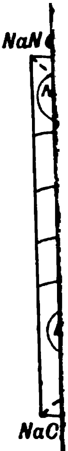


FIG. 123.







SHEET XV.

with the polythermal saturation curves, give the isothermal invariant points at the temperature which corresponds with that plane; and the intersections with the polythermal saturation surfaces give the isothermal saturation curves. In section I of Fig. 118, the two salts $AD + BC$ form the stable pair, and the curve of intersection PQ, of the plane with the saturation surface of $AD + BC$, is the isothermal saturation curve of these two salts. The diagonal AD, BC of this square section intersects the saturation curve PQ, and both isothermal invariant solutions P and Q are, therefore, congruently saturated. At the temperature of section II, the point Q falls on the line AD, BC, and below this temperature the line AD, BC will no longer intersect the saturation curve PQ, of $AD + BC$. The transition interval of the salt pair AD, BC extends, therefore, from the temperature of section II to the transition temperature. Section III is made at the temperature of the transition point S. In section IV, the two salts AB and CD form the stable reciprocal pair, and the curve UV is the intersection of the plane with the polythermal saturation surface of $AB + CD$; this salt pair must, naturally, also possess a transition interval. It can be seen that these isotherms, which are obtained by sections of the space figure, are identical with the series which we had already deduced in the previous paragraph.

It is, of course, possible that the reciprocal salt pairs may not possess a transition point in the temperature range within which saturated solutions can exist. In this case, one of the reciprocal pairs only will be capable of existing in stable equilibrium with solutions, and the number of possible isothermal types will be correspondingly limited. On the other hand, the isothermal relations may be complicated by the appearance of other binary or ternary compounds as solid phases in the system; some examples of more complicated quaternary systems formed by solutions of reciprocal salt pairs will be found in the next paragraph.

§ 76. In illustration of the theoretical types deduced in this chapter, we shall now describe the relations existing in some quaternary systems which have been investigated experimentally. The simplest quaternary isotherm which we have discussed (§ 51 *et seq.*) is that in which only three saturation surfaces appear. The system H_2O–$NaCl$–$BaCl_2$–$CuCl_2$ shows these simple relations at 30°.[1] At this temperature, the stable solid phases in the three binary systems H_2O–NaCl, H_2O–$BaCl_2$, and H_2O–$CuCl_2$ are NaCl, $BaCl_2.2H_2O$, and $CuCl_2.2H_2O$ respectively; neither hydrate suffers dehydration, nor does a binary or ternary compound appear, in the quaternary system. The quaternary isotherm shows only the three saturation surfaces of NaCl, of $BaCl_2.2H_2O$, and of $CuCl_2.2H_2O$. It is represented as a perpendicular projection of the space figure upon the base of the tetrahedron in Fig. 119, and as a perpendicular projection on a plane parallel to the opposite edges H_2O,NaCl and $CuCl_2$,$BaCl_2$ in Fig. 120. The saturation surfaces are marked in the figures with the corresponding solid phases, and it is seen that all three surfaces meet in the point *g*. This point represents, therefore, the isothermal invariant solution which is saturated at 30°, with the three solid salts NaCl, $BaCl_2$,$2H_2O$, and $CuCl_2.2H_2O$. We have shown in §§ 53 and 54 how these projections can be constructed from the analytical data, and we may exemplify the methods of construction by means of the solution *g*, the composition of which was found to be the following:

NaCl	$BaCl_2$	$CuCl_2$	H_2O per cent.
10·49	1·97	36·12	51·42

In order to find the position of the projection in Fig. 119, we must divide the concentration of the water equally between those of the three salts, when we obtain the following figures:

NaCl	$BaCl_2$	$CuCl_2$ per cent.
27·63	19·11	53·26

The point *g* in Fig. 119 gives the desired projection, and it is so chosen that it would represent a ternary mixture of the latter composition, if points in the triangle NaCl, $BaCl_2$, $CuCl_2$ represented ternary mixtures of these three salts, instead of, as is actually the case, projections of points representing quaternary mixtures.

The position of the projection *g* in Fig. 120 is defined by its perpendicular distance from the axis *O*, $CuCl_2$, which is equal to

$$\frac{H_2O - \text{NaCl per cent.}}{2} = \frac{51{\cdot}42 - 10{\cdot}49}{2} \quad 20{\cdot}46,$$

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[1] Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, 65, 586.

in the direction from O to H_2O; and by its perpendicular distance from the axis O, H_2O, which is equal to

$$\frac{CuCl_2 - BaCl_2 \text{ per cent.}}{2} = \frac{36{\cdot}12 - 1{\cdot}97}{2} = 17{\cdot}07,$$

in the direction from O to $CuCl_2$; the length of the diagonal of the square is, in this case, 100, and the above distances must be measured on this scale.

The system H_2O–NH_4Cl–$BaCl_2$–$CuCl_2$ at 30°[1] is complicated by the fact that a hydrated double salt occurs as a solid phase in the system. The composition of this ternary compound is given by the formula $CuCl_2.2NH_4Cl.2H_2O$, and solutions in equilibrium with it must, therefore, be represented by a saturation curve in the ternary system H_2O–NH_4Cl–$CuCl_2$, and by a saturation surface in the quaternary system. The isotherm is represented in perpendicular projection by Fig. 121; four saturation surfaces occur, and these are marked with the corresponding solid phases, the hydrated double salt being denoted by D. There are two quaternary invariant points L and K, which represent solutions saturated with

$$BaCl_2.2H_2O + NH_4Cl + D$$

and with

$$BaCl_2.2H_2O + CuCl_2.2H_2O + D$$

respectively. The two salts NH_4Cl and $CuCl_2.2H_2O$ are incompatible, both in the ternary and the quaternary systems, their saturation curves or surfaces being completely separated by the saturation curve or surface of the hydrated double salt. The point which represents this double salt is given by D in Fig. 121, and since it represents a ternary compound of H_2O, NH_4Cl and $CuCl_2$, the point lies in the triangle H_2O, NH_4Cl, $CuCl_2$. We may imagine that Fig. 121 represents the tetrahedron and the space isotherm as seen from above, the point H_2O being above the plane of the paper and the line H_2O, D lying on one of the inclined faces of the tetrahedron. Suppose now that a triangular section of the space figure is laid through the points H_2O, $BaCl_2$, and D. This section will clearly intersect only the saturation surfaces of $BaCl_2.2H_2O$ and of D, and the saturation curve LK of $BaCl_2.2H_2O + D$. The system H_2O–

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[1] Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, **66**, 687.

$BaCl_2$–$CuCl_2.2NH_4Cl.2H_2O$ is, therefore, a true ternary system, and it has been investigated as such at 30°.[1] This ternary system shows the saturation curves of $BaCl_2.2H_2O$ and of $CuCl_2.2NH_4Cl.2H_2O$ (*D*), and the isothermal invariant point which represents the solution saturated at 30° with $BaCl_2.2H_2O + D$. The saturation curve of $BaCl_2.2H_2O$ in this ternary system must give the curve of intersection of the plane H_2O, $BaCl_2$, *D* of Fig. 121, with the quaternary saturation surface of $BaCl_2.2H_2O$; the saturation curve of *D* must give the intersection of the plane with the quaternary saturation surface of *D*, and the ternary invariant point must give the point of intersection of the plane with the quaternary saturation curve *LK*.

It is clear that the isotherm is divided by the plane H_2O, $BaCl_2$, *D* into two parts, which can be considered as the isotherms, at this temperature, in two simpler quaternary systems. These two systems are H_2O–$BaCl_2$–NH_4Cl–*D* and H_2O–$BaCl_2$–$CuCl_2$–*D*, and they are represented one in each of the two tetrahedra into which the original tetrahedron is divided by the plane; both quaternary invariant solutions *L* and *K* are, in this case, congruently saturated.

The system H_2O–$(NH_4)_2SO_4$–$CuSO_4$–Li_2SO_4 at 30°[2], is still more complicated, since both the simple salts $CuSO_4$ and Li_2SO_4 form double salts with $(NH_4)_2SO_4$. In the ternary system H_2O–$(NH_4)_2SO_4$–Li_2SO_4, the anhydrous double salt $Li_2SO_4.(NH_4)_2SO_4$ occurs as a solid phase, and in the ternary system H_2O–$(NH_4)_2SO_4$–$CuSO_4$, the hydrated double salt $CuSO_4.(NH_4)_2SO_4.6H_2O$. The quaternary isotherm is given in Fig. 122, and it shows five saturation surfaces, those of the two double salts, and those of the three simple salts or their stable hydrates—$(NH_4)_2SO_4$, $Li_2SO_4.H_2O$, and $CuSO_4.5H_2O$. The double sulphate of lithium and ammonium is denoted in the figure by *LA*, and since it is an anhydrous salt, it is represented by a point on the line Li_2SO_4, $(NH_4)_2SO_4$. The double sulphate of copper and ammonium is denoted by *CA*, and since it is hydrated, it is represented by a point within the triangle H_2O, $CuSO_4$, $(NH_4)_2SO_4$. In the system H_2O–Li_2SO_4–$(NH_4)_2SO_4$, the ternary saturation curves *BE* and *CF*, of $Li_2SO_4.H_2O$ and $(NH_4)_2SO_4$, are separated by the saturation curve *EF* of the double salt *LA*; in the quaternary system the saturation surfaces of $Li_2SO_4.H_2O$ and $(NH_4)_2SO_4$ are similarly separated by that of the double salt *LA*. In the system H_2O–$CuSO_4$–$(NH_4)_2SO_4$, the ternary saturation curves *CG* and *AH*, of $(NH_4)_2SO_4$ and $CuSO_4.5H_2O$, are separated by the saturation curve *GH* of the hydrated double salt *CA*; in the quaternary system the saturation surfaces of $(NH_4)_2SO_4$ and $CuSO_4.5H_2O$ are similarly separated by that of *CA*. It can be seen from the figure that the intersection of the five saturation surfaces gives rise to seven quaternary saturation curves and three quaternary invariant points.

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[1] Schreinemakers, *loc. cit.*

[2] Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, **66**, 687.

The ternary system H_2O–Li_2SO_4–$CuSO_4$ is of the simplest type; it shows only the two saturation curves *BD* and *AD*, of $Li_2SO_4.H_2O$ and $CuSO_4.5H_2O$ and the single invariant point *D*, which represents the solution saturated with both these hydrates at the temperature of the isotherm. If increasing amounts of ammonium sulphate are added to the solution *D*, the two hydrates $Li_2SO_4.H_2O$ and $CuSO_4.5H_2O$ being retained as solid phases in equilibrium with the liquid, the point which represents the composition of the solution will traverse the quaternary curve *DK* of $CuSO_4.5H_2O + Li_2SO_4.H_2O$. Now at a certain stage formation of a double salt will begin and the question arises: Will the ammonium sulphate combine first with the lithium or the copper sulphate? This question is easily answered by means of Fig. 122, for the point *K* represents a solution saturated with $CuSO_4.5H_2O + Li_2SO_4.H_2O + CA$. When so much ammonium sulphate has been added that the composition of the solution is represented by the point *K*, the formation of the double sulphate of copper and ammonium will therefore begin. The composition of the solution cannot now alter on the addition of more ammonium sulphate, until the whole of the copper sulphate, present in the solid phase, has been converted into the double salt. Finally, however, when sufficient ammonium sulphate has been added, the whole of the copper sulphate will have been converted into the double salt, and only the two solid phases $Li_2SO_4.H_2O$ and *CA* will remain. If more ammonium sulphate is then added, the composition of the solution will again change, and the point which represents it will traverse the quaternary saturation curve *KL* of $Li_2SO_4.H_2O + CA$. When so much ammonium sulphate has been added that the composition of the solution is represented by the point *L*, the formation of the double sulphate of ammonium and lithium will begin. Since the liquid phase is now in equilibrium with the three solid phases $Li_2SO_4.H_2O + LA + CA$, its composition will remain unaltered on the addition of more ammonium sulphate, until sufficient has been added to convert the whole of the lithium sulphate, present as a solid phase, into the double sulphate of ammonium and lithium. When this has been done, again only two solid phases will remain, namely, the two double salts *CA* and *LA*. The continued addition of ammonium sulphate will then cause the point representing the composition of the solution to traverse the saturation curve *LM* of $CA + LA$, and, finally, when the composition of the solution is represented by the point *M*, the addition of ammonium sulphate will have no further effect upon this composition; since the point *M* represents the invariant solution which is saturated with the three solids $CA + LA + (NH_4)_2SO_4$, any ammonium sulphate which is added must remain unchanged as a solid phase. Thus, on the addition of ammonium sulphate to the solution *D*, the point representing the composition of the liquid phase must pass along the curves *DK*, *KL*, *LM* before the solution attains saturation with ammonium sulphate, and at the same time the hydrate $CuSO_4.5H_2O$, present as a solid phase, must be converted into the double salt *CA*, and the hydrate $Li_2SO_4.H_2O$ into the double salt *LA*.

Let us suppose next that a plane is laid through the points H_2O, Li_2SO_4, and *CA* of the space isotherm. It can be seen clearly from Fig. 122 that such a plane intersects only the saturation surfaces of $Li_2SO_4.H_2O$ and *CA*, and the saturation curve of $Li_2SO_4.H_2O + CA$. The system H_2O–Li_2SO_4–*CA* is, therefore, a ternary system. The double sulphate of lithium and ammonium does not appear as a solid phase in this system and lithium sulphate cannot, therefore, displace copper sulphate from its combination with ammonium sulphate. If, however, a plane is laid through the points H_2O, $CuSO_4$, *LA*, it will intersect, not only the saturation surfaces of $CuSO_4.5H_2O$ and *LA*, but also that of *CA*, as may be seen from the figure. The composition of the double salt *CA* cannot be expressed in terms of the three substances H_2O, $CuSO_4$, and *LA* alone, and the system H_2O–$CuSO_4$–*LA* is, therefore, not a ternary system; the double salt *LA*, of lithium and ammonium, is decomposed by copper sulphate with the formation of copper ammonium sulphate.

A complete section of this isotherm has been constructed by Schreinemakers, in which there is shown the intersection of the plane H_2O, $CuSO_4$, *LA*, not only with the saturation surfaces and curves, but also with the various complex spaces.[1]

The quaternary systems which we have so far discussed have been represented by perpendicular projections of the space isotherm, which is represented within a regular tetrahedron. The system H_2O–NaCl–KCl–$FeCl_2$ at 38°[2] is represented in Fig. 123 by Jänecke's method, which may also be considered as a perspective projection of the space isotherm represented within the tetrahedron (§ 56); the ternary invariant points lie on the sides of the triangle, and the ternary saturation curves are contained by these sides. The stable hydrate of ferrous chloride in the binary system H_2O–$FeCl_2$, at this temperature, is the tetrahydrate $FeCl_2.4H_2O$. Each of the ternary systems which form the basis of the quaternary system is of the simplest type, and shows only one isothermal invariant point at this temperature; the point *D* represents the ternary invariant solution saturated with NaCl + KCl, the point *E* that saturated with NaCl + $FeCl_2.4H_2O$, and the point *F* that saturated with KCl + $FeCl_2.4H_2O$. In the quaternary system, however, an anhydrous triple chloride $FeCl_2.3KCl.NaCl$ occurs as a solid phase (this triple salt is found in nature as the mineral rinneit). The quaternary saturation surface of rinneit is represented in Fig. 123 by the enclosed area *GHI*, and the composition of the ternary compound itself is given by the point *R*.

The quaternary system in which a triple salt occurs as a solid phase was discussed briefly in § 65, but the example represented in Fig. 123 shows some features of special interest.

A saturated solution which contains the three simple salts in the same proportion as they are contained by the triple salt is represented in the figure by the point *R*, and since this point lies on the saturation surface of KCl, such a solution is in equilibrium with potassium chloride, and not with rinneit itself. The triple salt rinneit is, therefore, decomposed by water with separation of potassium chloride, and the system H_2O–Rinneit is not a binary system ; if, for example, water is evaporated from an unsaturated solution of rinneit in water, the first salt to be deposited will be potassium chloride, and not rinneit. A solution which contains only rinneit, and which is in equilibrium with solid rinneit, if it can exist at all, is in a state of metastable, and not of stable, equilibrium. This metastable solution will, however, still be represented by the point *R* in Fig. 123, and the solution will be supersaturated with potassium chloride; the paths of crystallisation on the saturation surface of rinneit must, however, still radiate from the point *R* (*cf.* § 64), and if they are produced backwards in Fig. 123, they will be found to intersect in this point.

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[1] Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, **66**, 699.

[2] Boeke, *Sitzungsber. K. Akad. Wiss. Berlin*, 1909, **24**, 632.

Solutions the compositions of which can be expressed in terms of H_2O, NaCl, and rinneit, are represented in Fig. 123 by points on the line NaCl,*R*. This line does not intersect the saturation surface of rinneit, but only those of NaCl and KCl ; it is clear, therefore, that the system H_2O–NaCl–Rinneit is not a ternary system. Solutions which are in equilibrium with the two solid phases NaCl + Rinneit are represented by points on the quaternary saturation curve *GH*. This curve does not intersect the line NaCl,*R*, and a solution which contains only sodium chloride and rinneit cannot be in stable equilibrium with solid sodium chloride and solid rinneit. If such a solution exists at all, it is in a state of metastable equilibrium, and it will be represented by the point in which the saturation curve *HG* produced, intersects the line NaCl,*R*. The arrow-heads on this saturation curve, which is the path of crystallisation of solutions depositing sodium chloride and rinneit, must, therefore, be directed away from *G* and towards *H* along the whole length of the curve. It can be seen, in the same way, that the system H_2O–KCl–Rinneit is not a ternary system, and that the arrow-heads on the saturation curve *GI*, which is the path of crystallisation of solutions depositing both potassium chloride and rinneit, are directed away from *G* and towards *I* along the whole length of the curve.

The line $FeCl_2$,*R* intersects, besides the saturation surfaces of $FeCl.4H_2O$ and rinneit, the saturation surface of KCl. The system H_2O–$FeCl_2$–Rinneit, is again, not a ternary system, but the line $FeCl_2$, *R* does intersect, in the point *M*, the saturation curve *HI*, of $FeCl_2.4H_2O$ + Rinneit. A solution which contains only ferrous chloride and rinneit may, therefore, be in stable equilibrium with these two salts, and it is represented by the point *M*. The arrow-heads on the saturation curve *HI*, which is the path of crystallisation of solutions depositing both ferrous chloride tetrahydrate and rinneit, must be directed away from the point *M*, *i.e.*, they must be directed towards *H* on one side of the curve, and towards *I* on the other.

The quaternary invariant point *H* represents a solution saturated with the three solid phases

$$FeCl_2.4H_2O + NaCl + \text{Rinneit},$$

and it lies within the triangle $FeCl_2$, NaCl, *R*. It is, therefore, a congruently saturated solution, and the arrow-heads on the saturation curves which meet in this point show that it is a final drying-up point. The quaternary invariant point *I* represents a solution saturated with the three solid phases $FeCl_2.4H_2O$ + KCl + Rinneit. It is also a congruently saturated solution, and a final drying-up point. The quaternary invariant point *G* represents a solution saturated with the three solid phases NaCl + KCl + Rinneit, but it does not lie within the triangle NaCl, KCl, *R*. The solution *G* is incongruently saturated, and the arrow-heads show that the point *G* is not a final drying-up point.

Let us suppose that water is evaporated from a solution which is represented by a point on the saturation curve *DG*. The two salts NaCl and KCl will be deposited, and the point will traverse the curve until the composition of the solution is represented by the point *G*. At this point separation of solid rinneit will begin, and the composition of the solution will remain constant as long as the three solid phases NaCl, KCl, and rinneit are present. The arrow-heads on the saturation curves show, however, that the point representing the composition of the solution can move away from *G*, along either of the curves *GH* or *GI*, of NaCl + Rinneit or KCl + Rinneit. On the evaporation of water from the solution *G* in contact with the three solid phases NaCl, KCl, and rinneit, *both* the former must, therefore, be redissolved. If the relative weights of the three solid phases which are present is such that the sodium chloride is completely redissolved before the potassium chloride, then the point representing the composition of the solution will follow the saturation curve *GI* of KCl + Rinneit. The dissolution of solid potassium chloride will, however, continue during this stage of the evaporation, for the figure shows that the paths of crystallisation on the saturation surfaces of KCl and rinneit do not converge on the curve *GI*. If sufficient solid potassium chloride is present, the point representing the composition of the solution may follow the curve *GI* until the final drying-up point *I* is reached, but if sufficient of this salt is not present, it may be completely redissolved before the point *I* is reached. The point representing the composition of the solution will, in this case, leave the curve *GI*, follow a path of crystallisation on the saturation surface of rinneit, and reach a point on the saturation curve *HI*; if this point lies to the right of the line $FeCl_2,R$ the solution will dry finally at the constant composition given by the point *H*, if to the left of this line, then it will dry at the constant composition given by the point *I*.

It may happen that when water is evaporated from the solution *G* in contact with the three solid phases NaCl, KCl, and rinneit, the first solid phase to disappear is potassium chloride, and not, as we have just supposed, sodium chloride. In this case, the point representing the composition of the solution will follow the saturation curve *GH*, of NaCl + Rinneit. The incongruently saturated invariant solutions which we have previously discussed were characterised by the fact that their compositions could only be maintained constant by the dissolution of *one* of the solid phases with which they were in equilibrium. The composition of the incongruently saturated solution *G* can only be maintained constant, as we have seen, by the dissolution of *two* of the solid phases with which it is in equilibrium; such a solution is said to be doubly incongruent.

Let us now consider the behaviour of an unsaturated solution of rinneit when water is evaporated from it. We have already seen that the solution will first become saturated with potassium chloride, and it will then be represented by the point *R* of Fig. 123. This salt will therefore be deposited on the further removal of water, and the point representing the composition of the solution will traverse the path *RL*. When the composition is represented by the point *L*, separation of sodium chloride as a second solid phase will begin, and the point will follow the saturation curve *DG* of KCl + NaCl. When the composition of the solution is represented by the point *G*, separation of rinneit will begin, and the two salts potassium chloride and sodium chloride, which were deposited in the earlier stages of the evaporation, will simultaneously redissolve to maintain the constant composition of the solution. We have already shown that the subsequent path of crystallisation depends upon the proportion in which the two salts sodium chloride and potassium chloride are present in the solid phase.

In the present case, however, the original unsaturated solution contained the three simple salts, ferrous, potassium, and sodium chlorides, in the same proportion as they are contained by rinneit, and it follows that they must still be present in the correct proportion to form rinneit without leaving excess of any simple salt. The reaction which occurs at the invariant point *G* on the evaporation of water will therefore result, in this case, in the *simultaneous* disappearance of all three phases, Solution, KCl, and NaCl, and the solution will have dried completely when all salts are again combined in the form of solid rinneit.

Finally, we shall discuss briefly the polythermal conditions of equilibrium in this system. The triple salt rinneit possesses a transition point at 26·4°, and this transition point marks a lower temperature limit to its existence in the system. At the transition temperature, the four solid phases KCl, NaCl, $FeCl_2.4H_2O$, and rinneit are in equilibrium with an invariant solution, and as the temperature is lowered below 38°, the saturation surface *GHI*, of rinneit (Fig. 123), gradually decreases in area, the three invariant points *G*, *H*, and *I* approach one another, and at the transition temperature they coincide in the quaternary transition point, the saturation surface of rinneit being then represented by this point only. Below the transition temperature the quaternary isotherm is of the simplest type, and shows only the three saturation surfaces of KCl, NaCl, and $FeCl_2.4H_2O$.

If the temperature is raised above 38°, the saturation surface of a second ternary compound appears in the quaternary isotherm; this is the hydrated double chloride $FeCl_2.2KCl_2.2H_2O$, and it occurs in nature as the mineral douglasite. This ternary compound also possesses a transition point which is a lower limit to its existence as a solid phase, and the corresponding quaternary transition temperature is 38°. Above this temperature the saturation surface of douglasite appears, therefore, in the quaternary isotherm, and it is at first given by an enclosed triangular area surrounding the invariant point *I*; the solution *I*, which is in equilibrium with the three solids $FeCl_2.4H_2O$ + KCl + Rinneit, ceases, therefore, to exist as a stable phase, being replaced by three others which are formed by the intersection of the douglasite saturation surface with the three saturation curves *FI*, *GI*, and *HI*. As the temperature is raised, the saturation surface of douglasite rapidly grows, and it reaches the side $FeCl_2$, KCl of the triangle at the transition temperature of the hydrated double salt in the ternary system H_2O–$FeCl_2$–KCl; this ternary transition temperature is 38·3°, and it is but slightly higher than the quaternary transition temperature. Above this point the saturation curve of douglasite will appear in the ternary system H_2O–$FeCl_2$–KCl, and the quaternary saturation surfaces of $FeCl_2.4H_2O$ and KCl will then be completely separated from each other. This system offers an example of the isothermal types which occur in the neighbourhood of the transition point, when a hydrated double salt appears as a solid phase; these types were discussed theoretically in § 65.

The majority of quaternary systems which have been investigated are formed by solutions of reciprocal salt pairs; such systems are often of considerable practical importance. The system H_2O–$(\overset{+}{Na}, \overset{+}{K})$–$(\overset{-}{NO_3}, \overset{-}{Cl})$ has been very thoroughly investigated,[1] and the isotherms at four different temperatures are represented by Jänecke's method, in one diagram, in Fig. 124. The only solid phases which appear are the four salts $NaNO_3$, KNO_3, NaCl, and KCl, and the system is, therefore, of the simple type discussed in § 71 and the following paragraphs. It can be seen from Fig. 124 that at all four temperatures the two salts NaCl and KNO_3 are compatible. The saturation surfaces of these salts intersect in the curve P_1P_2, the points of which represent, therefore, solutions saturated with this stable salt pair. The saturation surfaces of KCl and $NaNO_3$ are completely separated from each other, and these two salts are incompatible, or form the unstable pair. The point P_1 represents the isothermal invariant solution which is saturated with the salt triad $NaCl + KNO_3 + NaNO_3$. At every temperature, it lies within the triangle NaCl, KNO_3, $NaNO_3$, and is, therefore, congruently saturated. The point P_2 represents the isothermal invariant solution which is in equilibrium with the three solid salts $NaCl + KNO_3 + KCl$. At 0° this point lies within the triangle NaCl,KNO_3, KCl, and represents, therefore, a congruently saturated solution. At 25°, the point P_2 lies on the line NaCl, KNO_3, and above this temperature it falls outside the triangle NaCl, KNO_3, KCl. The stable salt pair enters its transition interval, therefore, at 25°, and at temperatures above this the invariant solution P_2 is incongruently saturated (*cf.* § 74).

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[1] Reinders, *Zeitsch. anorg. Chem.*, 1915, **93**, 202.

As an example of the practical use of these isotherms, let us suppose that it is desired to make potassium nitrate from sodium nitrate and potassium chloride. The composition of a salt mixture containing equimolecular quantities of the two salts $NaNO_3$ and KCl may be expressed in the following form for the purpose of Jänecke's representation:

$$50\overset{+}{Na},\ 50\overset{+}{K},\ 50\overset{-}{NO_3},\ 50\overset{-}{Cl},$$

where the sum of the concentrations of the positive ions, expressed in equivalents, and therefore also of the negative ions, is equal to 100. In accordance with the graphical method of representation deduced in § 68, the side of the square in Fig. 124 must be taken to represent 100, the concentration of the ion Na (50) must be measured from the side KNO_3,KCl, and that of the ion NO_3 (50) from the side NaCl,KCl. The salt mixture the composition of which is given above will be represented, therefore, by the point *a*, in which the diagonals of the square intersect; it is clear that the distances of this point from the side $NaNO_3$,NaCl, and from the side $NaNO_3$, KNO_3, will also be equal to 50, *i.e.*, the concentrations of the ions $\overset{+}{K}$ and $\overset{-}{Cl}$ in the salt mixture are also correctly represented. It can be seen from the figure that the point *a* lies, at 100°, on the saturation surface of NaCl, and if water is evaporated at

100° from an unsaturated solution containing equimolecular amounts of sodium nitrate and potassium chloride, the solution will, therefore, first become saturated with sodium chloride. On the continued removal of water, sodium chloride will be deposited, and the point representing the composition of the solution will follow the path of crystallisation NaCl, *b*, which passes through *a*. When the composition of the solution is given by the point *b*, the solution will be just saturated with potassium chloride also. Since it is our object to separate the potassium in the form of nitrate, we must stop the evaporation when the solution has reached this composition, and remove the sodium chloride by filtration at 100°. The composition of the salt mixture contained in the filtered solution is represented by the point *b*, and this point lies, in the 0° isotherm, on the saturation surface of KNO_3. If the filtered solution is cooled to 0° it will, therefore, deposit potassium nitrate, either spontaneously, or on the evaporation of water at 0°; we cannot tell simply by an examination of the diagram whether the solution filtered at 100° will be unsaturated when it is cooled to 0°, or whether, as seems more probable, it will be supersaturated with potassium nitrate. If the latter is the case, then spontaneous crystallisation of potassium nitrate will occur, and the point representing the composition of the solution will traverse the path of crystallisation KNO_3, *c*, which passes through *b*. In any case, by the evaporation of water if necessary, we can cause the solution to deposit pure potassium nitrate until its composition is represented by the point *c*. Further than this we must not go, since the solution will then be just saturated with sodium chloride also, and continued crystallisation will result in the deposition of this salt with the potassium nitrate. We can determine whether it will be necessary to evaporate water by the following simple calculation, which will give us, at the same time, the amount of potassium nitrate deposited.

The composition of the solution *b*, saturated at 100° with NaCl + KCl, expressed in equivalent of the ions, is

$$59\overset{+}{K},\ 41\overset{+}{Na},\ 59\overset{-}{NO_3},\ 41\overset{-}{Cl},\ 283H_2O,$$

or, expressed as moles of the salts,

$$59KNO_3,\ 41NaCl,\ 283H_2O.$$

VI

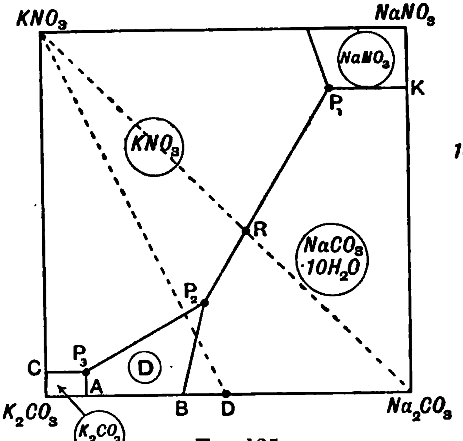
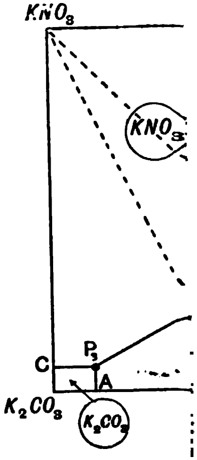


FIG. 125.

10°



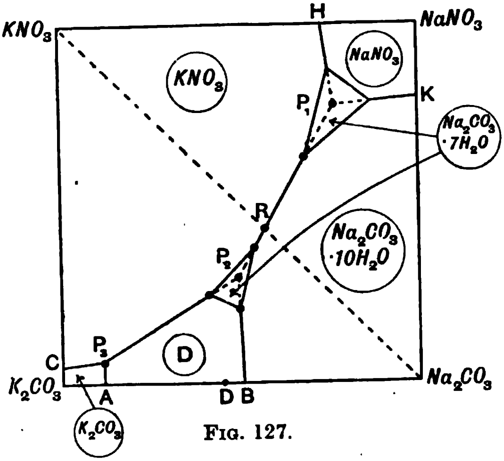
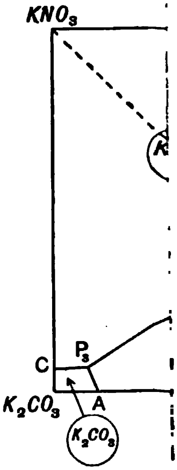


FIG. 127.



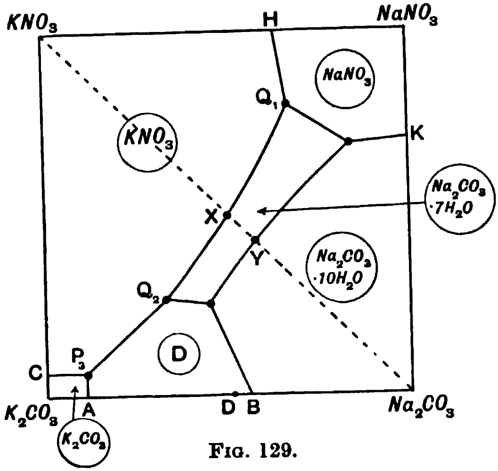
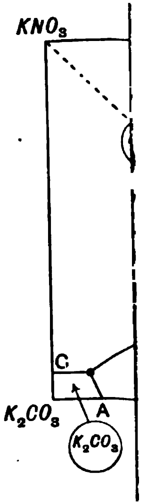


FIG. 129.



SHEET XVI.

The composition of the solution *c*, saturated at 0° with $KNO_3 + NaCl$, is

$$23{\cdot}5\overset{+}{K},\ 76{\cdot}5\overset{+}{Na},\ 23{\cdot}5\overset{-}{NO_3},\ 76{\cdot}5\overset{-}{Cl},\ 640H_2O,$$

or

$$23{\cdot}5KNO_3,\ 76{\cdot}5NaCl,\ 640H_2O.$$

We will suppose that, in passing from the solution *b* at 100°, *y* parts of potassium nitrate are deposited and *z* parts of the solution *c* are formed at 0°; further, we will suppose that in order to do this, *x* parts of water must be evaporated from the solution at 0°. We have then the following mathematical identity:

$$\underset{\text{Solution } b.}{(59KNO_3, 41NaCl, 283H_2O)} =$$

$$xH_2O + yKNO_3 + z\underset{\text{Solution } c.}{(23{\cdot}5KNO_3, 76{\cdot}5NaCl, 640H_2O)}$$

Since the total amounts of potassium nitrate, of sodium chloride, and of water, on the left side of this equation, must be equal respectively to the total amounts of these substances, on the right side, we have

$$\begin{array}{ll} \text{for } KNO_3 & 59 = y + 23{\cdot}5z \\ \text{for } NaCl & 41 = 76{\cdot}5z \\ \text{for } H_2O & 283 = x + 640z, \end{array}$$

and therefore,

$$x = -60, \qquad y = 46{\cdot}4, \qquad z = 0{\cdot}536.$$

We see that *x*, the amount of water to be evaporated, is negative. This clearly means that the original solution, filtered from sodium chloride at 100°, is supersaturated to such an extent at 0° that if the crystallisation is to stop when the composition of the solution is represented by the point *c*, water must actually be added to it in the proportion of 60 moles for every 100 moles of the total salts. If this water is not added, the crystallisation will continue after the composition of the solution has reached the value given by the point *c*, and the potassium nitrate will then be contaminated with sodium chloride. The amount of potassium nitrate deposited during the cooling is given by *y*, which is equal to 46·4. Of the 59 moles of potassium which were contained in the original solution, 46·4 moles have been separated, therefore, as pure solid potassium nitrate; the yield is 78·7 per cent.

The system H_2O–($\overset{+}{Na_2}$, $\overset{+}{K_2}$)–($\overset{-}{[NO_3]_2}$, $\overset{-}{CO_3}$)[1] is not quite so simple in type as the system which we have just discussed. The isotherm at 10° is represented diagrammatically, by Jänecke's method, in Fig. 125, although it is represented in the original publication as a perpendicular projection of the space isotherm referred to a pyramid. The isotherm is complicated by the fact that a ternary compound, namely, the hydrated double carbonate $Na_2CO_3.K_2CO_3.6H_2O$, occurs as a solid phase in the ternary system H_2O–Na_2CO_3–K_2CO_3, and the quaternary isotherm shows, therefore, the saturation surface of this compound. The ternary systems H_2O–Na_2CO_3–K_2CO_3 is represented on the side Na_2CO_3,K_2CO_3 of the square in Fig. 125, and it shows, at this temperature, two invariant points A and B, which represent solutions saturated with $K_2CO_3 + D$ and $Na_2CO_3.10H_2O + D$ respectively, where the hydrated double salt Na_2CO_3,$K_2CO_3.6H_2O$ is denoted by D. The stable solid phase in the binary system H_2O–Na_2CO_3, at the temperature of the isotherm, is the decahydrate $Na_2CO_3.10H_2O$, and the ternary saturation curve of this hydrate in the system H_2O–Na_2CO_3–K_2CO_3 is contained by the side Na_2CO_3,K_2CO_3 of the square, and is represented by the straight line Na_2CO_3,B. The ternary saturation curve of the hydrated double salt in this system is represented, similarly, by the line BA, and that of potassium carbonate, which occurs as an anhydrous salt, is represented by the straight line K_2CO_3,A. The composition, expressed in molecular percentages, of the salt mixture contained by the ternary compound $Na_2CO_3.K_2CO_3$,$6H_2O$ is

$$50Na_2CO_3,50K_2CO_3,$$

and the point D, which represents this compound in Fig. 125, bisects, therefore, the side Na_2CO_3,K_2CO_3 of the square. Since points in Fig. 125 represent only the composition of the salt mixtures contained in saturated solutions, the point D also represents the saturated solution which contains the simple salts in the same proportion as does the double salt. This saturated solution is not, however, in equilibrium with the solid double salt, for the point D lies on the ternary saturation curve Na_2CO_3,B, of sodium carbonate decahydrate. The double salt is, therefore, decomposed by water, and the ternary invariant solution B is incongruently saturated.

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[1] Kreman, *Monats.* 1909, **30**, 311.

The three remaining ternary systems are all of the simplest type, and they are represented one on each of the three remaining sides of the square; the figure shows that only one isothermal invariant solution exists in each of these systems.

The quaternary isotherm contains five saturation surfaces—those of the five salts (four simple salts and one hydrated double salt) which can occur as solid phases; the intersections of these surfaces form seven saturation curves, and these curves intersect, in groups of three, in the three quaternary invariant points P_1, P_2, and P_3. It can be seen from the figure that the two salts KNO_3 and Na_2CO_3—the latter in the form of its decahydrate—constitute the stable pair, and solutions saturated with this salt pair are represented by points on the saturation curve P_1P_2. In regions representing solutions of comparatively high potassium carbonate content, the saturation surface of sodium carbonate is displaced by that of the double carbonate, and in these regions potassium nitrate and the double carbonate form the compatible salts; solutions saturated with these two are represented by points on the saturation curve P_2P_3.

The diagonal KNO_3, Na_2CO_3 of the square in Fig. 125 intersects only the saturation surfaces of KNO_3 and $Na_2CO_3.10H_2O$, and the saturation curve of P_1P_2, of $KNO_3 + Na_2CO_3.10H_2O$. The system H_2O–KNO_3–Na_2CO_3, which is formed by water and the stable reciprocal pair, is, therefore, a ternary system, and the point R represents the corresponding ternary invariant solution. The isotherm is divided by the line KNO_3,Na_2CO_3 into two parts, which give the isotherms in two simpler quaternary systems. The system H_2O–KNO_3–Na_2CO_3–$NaNO_3$ is represented at this temperature, within the triangle KNO_3,Na_2CO_3, $NaNO_3$, and it shows only the three saturation curves RP_1, KP_1, and HP_1, and the single isothermal invariant point P_1; the isotherm in this system is of the simplest type and may be compared with Fig. 82. The isothermal relations in the system H_2O–KNO_3–Na_2CO_3–K_2CO_3 are represented within the triangle KNO_3, Na_2CO_3, K_2CO_3. The hydrated double salt occurs as a solid phase in this quaternary system, and its saturation surface appears in the isotherm; the latter contains two isothermal invariant points P_2 and P_3, and it can be compared with Fig. 102, where a quaternary system of the same type is represented within an equilateral triangle instead of, as in the present case, a right-angled isosceles triangle.

The isotherm in this system at a temperature of 24·2° is considerably more complicated. It is represented diagrammatically in Fig. 126. It can be seen that the hydrated double salt still appears as a solid phase in the system, but the point *D* now lies on the ternary saturation curve *BA*, of the double salt, and the latter is, therefore, no longer decomposed by water; at a temperature between 24·2° (Fig. 126) and 10° (Fig. 125) the point *B* must coincide with the point *D*, and this temperature will mark the beginning of the transition interval of the hydrated double salt. The isotherm at 24·2° differs from that at 10° in the further respect that two additional saturation surfaces appear, those of the two hydrates $Na_2CO_3.7H_2O$ and $Na_2CO_3.H_2O$. The first of these extends into the side Na_2CO_3,$NaNO_3$ of the square and the ternary system H_2O–Na_2CO_3–$NaNO_3$ shows, therefore, in addition to the saturation curve Na_2CO_3,*F*, of the decahydrate $Na_2CO_3.10H_2O$, the saturation curve *FG* of the heptahydrate $Na_2CO_3.7H_2O$. The saturation surface of the monohydrate $Na_2CO_3.H_2O$ lies wholly within the square.

In order to make these quaternary isothermal relations clearer, we will first consider the conditions of equilibrium in the binary system H_2O–Na_2CO_3. There are two transition points in this system, corresponding with temperatures of 31·85° and 37°. At the first of these, the two hydrates $Na_2CO_3.10H_2O + Na_2CO_3.7H_2O$ are in equilibrium with a binary invariant solution; it is the binary transition point of the decahydrate, and the stable solid phase in equilibrium with binary solutions below 31·85° is the decahydrate $Na_2CO_3.10H_2O$, above 31·85° the heptahydrate $Na_2CO_3.7H_2O$. The point Na_2CO_3 in the quaternary isotherm at 24·2° (Fig. 126) represents, therefore, a binary solution in equilibrium with the decahydrate, and it lies on the boundary of the quaternary saturation surface of $Na_2CO_3.10H_2O$.

At the ternary transition point of the decahydrate in the system H_2O–Na_2CO_3–$NaNO_3$, the three solid phases

$$Na_2CO_3.10H_2O + Na_2CO_3{\cdot}7H_2O + NaNO_3$$

are in equilibrium with a ternary invariant solution ; the corresponding transition temperature will mark a lower temperature limit to the existence of the heptahydrate as a solid phase *in the ternary system*, just as the binary transition temperature is a lower temperature limit to its existence *in the binary system.* We have shown in § 44 that the binary transition temperature of a hydrate is lowered by the addition of a third component, and it can in fact be seen that the heptahydrate occurs as a solid phase in the system H_2O–Na_2CO_3–$NaNO_3$ at 24·2°, since its ternary saturation curve *FG* appears in the isotherm. The transition temperature of the deca- to the hepta-hydrate has, therefore, been lowered from 31·85° in the binary system, to a temperature below 24·2° in the ternary system H_2O–Na_2CO_3–$NaNO_3$; the exact value of this ternary transition temperature has not been determined.

At the second transition point (37°) in the binary system H_2O–Na_2CO_3, the two hydrates $Na_2CO_3.7H_2O + Na_2CO_3.H_2O$ are in equilibrium with a binary invariant solution ; it is the binary transition point of the heptahydrate. Between the temperatures 31·85° and 37° the heptahydrate is the stable solid phase in equilibrium with binary solutions, whilst above 37° the monohydrate is the stable phase. The ternary transition point of the heptahydrate in the system H_2O–Na_2CO_3–$NaNO_3$ must be lower than 37°, but it is clearly not so low as 24·2°, since the quaternary saturation surface of the monohydrate in Fig. 126 does not extend into the side Na_2CO_3,$NaNO_3$ of the square. The monohydrate can, however, exist as a stable solid phase in equilibrium with quaternary solutions, and the transition point of the hepta- to the mono-hydrate has been lowered, therefore, from 37° in the binary system, to a temperature below 24·2° in the quaternary system.

We discussed in § 58 the way in which the saturation surface of a salt hydrate appears in the quaternary isotherm, in the neighbourhood of its quaternary transition point ; we saw that it appears first at the invariant point in the isotherm at the transition temperature, and that it grows out from this point as the temperature is altered. We will consider some of the transition forms which the isotherm may show in passing from the type represented in Fig. 125 to that represented in Fig. 126; the transition forms between 10° and 24·2° have not been experimentally investigated, but they can be deduced by the methods used in § 58.

Let us suppose that the temperature, in the system

$$H_2O\text{–}(\overset{+}{Na_2}, \overset{+}{K_2})\text{–}(\overset{-}{[NO_3]_2}, \overset{=}{CO_3}),$$

is slowly raised from 10°. The isotherm at this temperature is given by Fig. 125, and we have seen that it is divided by the line KNO_3,Na_2CO_3 into two parts, which can be considered as the isotherms at 10°, in the two quaternary systems

$$H_2O\text{–}KNO_3\text{–}Na_2CO_3\text{–}NaNO_3 \text{ and } H_2O\text{–}KNO_3\text{–}Na_2CO_3\text{–}K_2CO_3.$$

On raising the temperature we shall reach, first, the transition temperature of the decahydrate in one of these quaternary systems. We will assume that the transition temperature in the system H_2O–KNO_3–Na_2CO_3–$NaNO_3$ is first attained, and the isotherm immediately above this temperature will then contain the saturation surface of the heptahydrate intersecting the saturation curves HP_1, KP_1, and RP_1, around their common point of intersection, as shown in Fig. 127. If, on a further increase in the temperature, the quaternary transition point of the decahydrate in the system H_2O–KNO_3–Na_2CO_3–K_2CO_3 is next reached, the saturation surface of the heptahydrate will appear in the triangle KNO_3, Na_2CO_3, K_2CO_3 surrounding the point P_2, as shown in Fig. 127. When the temperature is raised still higher, the saturation surfaces of the heptahydrate will grow, and eventually they will touch one another in a point V, on the line KNO_3,Na_2CO_3, as shown in Fig. 128. The point V represents a solution in equilibrium with the three solid phases $Na_2CO_3.10H_2O + Na_2CO_3.7H_2O + KNO_3$, and since it lies on the diagonal KNO_3, Na_2CO_3, the point represents a solution in the ternary system H_2O–KNO_3–Na_2CO_3, which is formed by water and the stable reciprocal salt pair. It is the ternary transition point of the decahydrate in this system, and at higher temperatures the two saturation surfaces of the heptahydrate, which touch one another in the single point V of

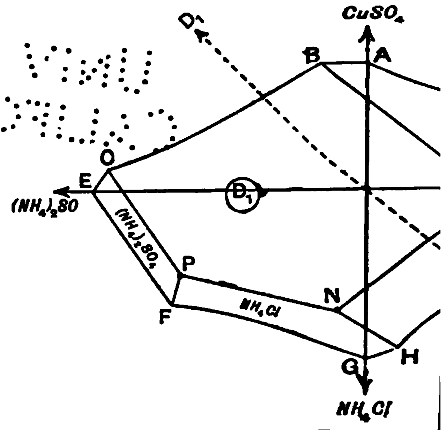

Fig. 131.

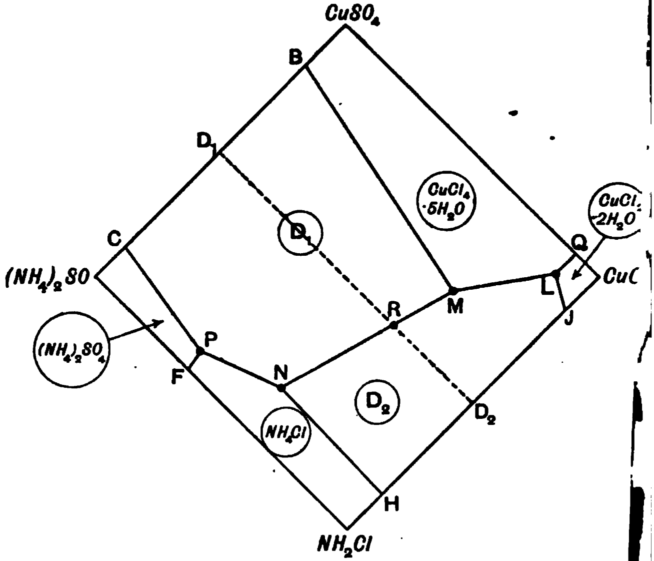

Fig. 132.

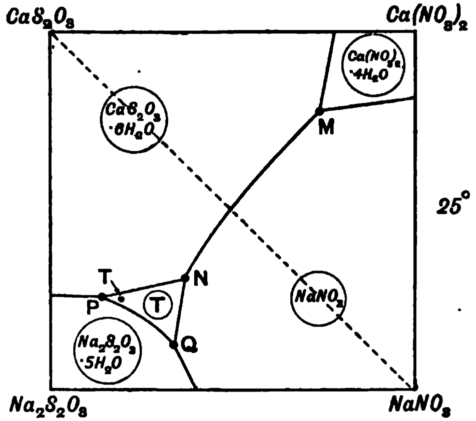

Fig. 134.

SHEET XVII.

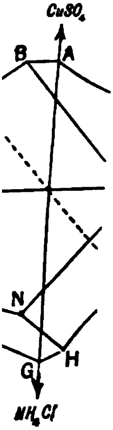

FIG. 131.

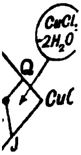

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Fig. 127, will coalesce into one continuous saturation surface, as shown in Fig. 129. This surface intersects the diagonal KNO_3, Na_2CO_3 in the line XY, which represents the saturation curve of the heptahydrate in the ternary system H_2O–Na_2CO_3–KNO_3.

If the next transition temperature which is reached when the temperature is further raised is that of the decahydrate in the ternary systems H_2O–Na_2CO_3–$NaNO_3$, the next isothermal type will be that represented in Fig. 130. The saturation surface of the heptahydrate has reached the side $Na_2CO_3,NaNO_3$ of the square, and its boundary line FG, in this side, is the ternary saturation curve of the heptahydrate in the system H_2O–Na_2CO_3–$NaNO_3$.

Finally, on further increasing the temperature, we shall reach the quaternary transition points of the heptahydrate, and at temperatures above these the saturation surfaces of the monohydrate will appear in the isotherm ; they are represented by the dotted lines surrounding the isothermal invariant points Q_1 and Q_2 in Fig. 130. These surfaces will grow and ultimately combine to form one continuous saturation surface, exactly as did the saturation surfaces of the heptahydrate at lower temperatures. This will give rise to the isothermal type represented in Fig. 126, which has been experimentally verified. The three ternary systems H_2O–Na_2CO_3–K_2CO_3, H_2O–$NaCO_3$–$NaNO_3$, and H_2O–Na_2CO_3–KNO_3 are represented on the two sides Na_2CO_3,K_2CO_3; $Na_2CO_3,NaNO_3$, and the diagonal Na_2CO_3, KNO_3 respectively in Fig. 126. In the first of these, sodium carbonate can only occur as a solid phase in the form of its decahydrate; the saturation curve of the decahydrate in this system is represented by the line Na_2CO_3,B. In the second ternary system, sodium carbonate can occur as a solid phase in the form of both the deca- and the heptahydrate; the saturation curve of the decahydrate in this system is represented by the line Na_2CO_3,F, and that of the heptahydrate by the line FG. In the third ternary system, the deca-, the hepta-, and the mono-hydrate of sodium carbonate can all occur as solid phases; the saturation curve of the decahydrate is represented by the line Na_2CO_3,Y, that of the heptahydrate by the line YX, and that of the monohydrate by the line XZ.

The system $H_2O–(\overset{+}{Cu},\overset{+}{[NH_4]_2})–(\overset{-}{SO_4},\overset{-}{Cl_2})$[1] at 30° is represented in Fig. 131 as a perpendicular projection of the space isotherm upon the base of the pyramid (*cf.* § 72), and in Fig. 132 by Jänecke's method; the reader can compare the two methods of representation by means of these figures, and to render this comparison easy the square in Fig. 132 is drawn in such a position that its diagonal, and not as usual its side, is parallel to the edge of the paper. The perpendicular projection (Fig. 131) possesses the advantage of showing somewhat more clearly the relations in the ternary systems which form the basis of the quaternary system. In Jänecke's representation (Fig. 132), the ternary saturation curves are contained by the straight sides of the square, but in the perpendicular projection they form a framework within which are to be found the quaternary saturation curves and surfaces. The complete square is not shown in Fig. 131, but only that part of it which contains the various saturation surfaces; the directions in which the corners of the square lie, are shown, however, by the arrow-heads.

The ternary saturation curves in the system $H_2O–CuSO_4–(NH_4)_2SO_4$ are given by the boundary curves *AB*, *BC*, and *CE* in the corresponding quadrant of Fig. 131. There occurs, besides the saturation curves *AB* and *CE* of the simple salts, that of the hydrated double sulphate $CuSO_4.(NH_4)_2SO_4.6H_2O$, which we will denote by D_1. In the same way, the ternary isotherm in the system $H_2O–CuCl_2–NH_4Cl$ contains the saturation curve *HJ* of the hydrated double chloride $CuCl_2.2NH_4Cl.2H_2O$, which we will denote by D_2. The two remaining ternary systems are of the simplest type at this temperature, and the isotherms contain only the saturation curves of the simple salts or their stable hydrates. The quaternary isotherm shows, therefore, six saturation surfaces, those of four simple salts (or their hydrates) and those of two hydrated double salts. It can be seen from the figure that neither the salt pair

$$CuSO_4.5H_2O + NH_4Cl$$

nor the salt pair

$$CuCl_2.2H_2O + (NH_4)_2SO_4$$

can exist in stable equilibrium with solutions, since the corresponding saturation surfaces are completely separated by those of the two double salts; these two are, however, compatible, and solutions in equilibrium with them are represented by points on the saturation curve *MN*. The points, in Fig. 131, which represent the compositions of the two double salts are outside the picture, but the line which joins them is shown dotted in the figure, and the directions in which they lie are indicated by the arrow-heads. It can be seen that the line joining the points which represent the two double salts intersects only the saturation surfaces of these salts and the saturation curve *MN* of $D_1 + D_2$. The system formed by water and the two double salts is, therefore, a ternary system.

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[1] Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, **69**, 557.

It can be seen equally clearly from Jänecke's representation (Fig. 132) that the system $W\text{–}D_1\text{–}D_2$ is a ternary system, and this figure also shows very clearly that the isotherm is divided by the line D_1D_2, into two parts which give the isothermal relations in two simpler systems. The part of the isotherm which lies within the rectangle D_1, D_2, $CuCl_2$, $CuSO_4$ can be considered as giving the conditions of equilibrium in the system.

$$\mathrm{H_2O\text{–}CuSO_4\text{–}CuSO_4.(NH_4)_2SO_4\text{–}CuCl_2\text{–}CuCl_2.(NH_4Cl)_2}$$

or $$\mathrm{H_2O\text{–}(\overset{+}{Cu}_2,\ Cu[\overset{+}{NH_4}]_2)\text{–}(\overset{-}{Cl}_4,[\overset{-}{SO_4}]_2)}.$$

The relations are clearly those which occur in a system formed by solutions of reciprocal salt pairs where only the four simple salts occur as solid phases. The compatible salts are $CuSO_4.5H_2O$ and D_2, but the invariant solution *M*, which is in equilibrium with $CuSO_4.5H_2O + D_2 + D_1$, is incongruently saturated. The part of the isotherm which lies within the rectangle D_1, D_2, NH_4Cl, $(NH_4)_2SO_4$, can be considered as giving the conditions of equilibrium in the system.

$$\mathrm{H_2O\text{–}(NH_4)_2SO_4\text{–}CuSO_4.(NH_4)_2SO_4\text{–}NH_4Cl\text{–}CuCl_2.(NH_4Cl)_2}$$

or $$\mathrm{H_2O\text{–}([\overset{+}{NH_4}]_4,\ Cu[\overset{+}{NH_4}]_2)\text{–}(\overset{-}{Cl}_4,[\overset{-}{SO_4}]_2)}.$$

This system also behaves like that formed by solutions of reciprocal salt pairs of the simplest type. The compatible salts are here $NH_4Cl + D_1$ and the invariant solution *N*, which is in equilibrium with $NH_4Cl + D_1 + D_2$, is also incongruently saturated.

The system H_2O–$(\overset{+}{Na_2}, \overset{+}{Ca})$–$(\overset{-}{S_2O_3}, [\overset{-}{NO_3}]_2)$[1] is represented at 9° and 25° in Figs. 133 and 134, respectively. There appear, as solid phases in this system, the four simple salts or their stable hydrates :

$$NaNO_3,\ Ca(NO_3)_2.4H_2O,\ CaS_2O_3.6H_2O \text{ and } Na_2S_2O_3.5H_2O,$$

and the triple salt :

$$NaNO_3.CaS_2O_3.Na_2S_2O_3.11H_2O,$$

which we will denote by the symbol T. It can be seen that this triple salt is hydrated, and its composition can, therefore, only be expressed completely in terms of four components, namely, three simple salts and water. It is, in other words, a quaternary compound, and it can only appear as a solid phase in equilibrium with quaternary solutions ; an anhydrous triple salt is a ternary compound, and it can appear as a solid phase in equilibrium with liquids in the ternary system formed by the anhydrous salts alone.

We will consider, first, the isotherm at 25° (Fig. 134). The two salts $CaS_2O_3.6H_2O$ and $NaNO_3$ form the stable reciprocal pair, and solutions which are in equilibrium with this salt pair are represented by points on the saturation curve MN. The diagonal CaS_2O_3, $NaNO_3$ intersects only the saturation surfaces of calcium thiosulphate and sodium nitrate, and the curve MN, the points of which represent solutions saturated with both these salts. The system formed by water and the stable salt pair is, therefore, a ternary system, and the line CaS_2O_3,$NaNO_3$ divides the isotherm into two parts, which give the isothermal relations in two simpler quaternary systems. The system H_2O–CaS_2O_3–$NaNO_3$–$Ca(NO_3)_2$ is represented within the triangle CaS_2O_3, $NaNO_3$, $Ca(NO_3)_2$, and it is of the simplest type, showing only one isothermal invariant point M, which represents a solution saturated with the three simple salts or their stable hydrates. The system H_2O–CaS_2O_3–$NaNO_3$–$Na_2S_2O_3$ is represented within the triangle CaS_2O_3, $NaNO_3$, $Na_2S_2O_3$, and the isotherm shows, besides the saturation surfaces of these three salts, that of the triple salt which is formed by the union of all three. The isotherm belongs to the type which we discussed in § 65 and which is illustrated (as a perpendicular projection) in Fig. 103; we have already given one example of a quaternary system in which a triple salt (rinneit) occurs as a solid phase. The point *T* in Fig. 134 represents the composition of the triple salt, and since it lies on the saturation surface of the triple salt, it follows that a saturated solution containing the simple salts in the same proportion as does the triple salt is in equilibrium with the solid triple salt. The latter is, therefore, not decomposed by water, and the system H_2O–Triple salt behaves, at the temperature of the isotherm, as a true binary system; the triple salt which occurs in this system differs, in this respect, from rinneit.

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[1] Kremann and Rodemund, *Zeit. anorg. Chem.*, 1914, **86**, **373**.

In the isotherm at 9° (Fig. 133), the two salts $CaS_2O_3.6H_2O$ and $NaNO_3$ still form the stable reciprocal pair, but the system formed by water and this salt pair is no longer a ternary system. The saturation surface of the triple salt has grown to such an extent on lowering the temperature that at 9° it intersects the diagonal CaS_2O_3, $NaNO_3$; the triple salt appears, therefore, as a solid phase in the system H_2O–CaS_2O_3–$NaNO_3$, which is no longer ternary. The point *T*, which represents the composition of the triple salt, still lies on the saturation surface *NPQ* of that salt, and the system H_2O–Triple salt still behaves, therefore, as a true binary system.

The rapid decrease in the area of the saturation surface of the triple salt as the temperature is raised suggests that this salt possesses an upper stability limit. This is actually the case, and the transition point of the triple salt is reached at 29°. At this temperature the triple salt and the three constituent simple salts are all in equilibrium with an invariant solution, and above this temperature the simple salts alone appear as solid phases in the system; the isotherm is then of the simple type illustrated by Fig. 115.

We shall conclude these examples with a brief description of four quaternary systems which are of great importance for the study of the oceanic salt deposits. The principle constituents of sea water are the chlorides and sulphates of the three metals, sodium, potassium and magnesium. The system formed by water and these salts can be represented by the notation:

$$H_2O\text{–}(\overset{+}{Na_2},\overset{+}{K_2},\overset{+}{Mg})\text{–}(\overset{-}{Cl_2},\overset{-}{SO_4});$$

it is a system of five, and not of four, components. The basis of this system is given, however, by a number of quaternary systems, and these are formed by water and all possible combinations of the five ions taken four at a time. There are, for example, two quaternary systems which can be formed from water, three positive ions, and one negative ion. These systems are:

$$H_2O\text{–}(\overset{+}{Na_2},\overset{+}{K_2},\overset{+}{Mg})\text{–}\overset{-}{Cl_2}$$

and $$H_2O\text{–}(\overset{+}{Na_2},\overset{+}{K_2},\overset{+}{Mg})\text{–}\overset{-}{SO_4},$$

or, as we have generally written:

$$H_2O\text{–}NaCl\text{–}KCl\text{–}MgCl_2$$

and $$H_2O\text{–}Na_2SO_4\text{–}K_2SO_4\text{–}MgSO_4.$$

They are systems formed by water and three salts with a common ion, a type of quaternary system which we discussed in § 51 and the succeeding paragraphs. There are, on the other hand, three quaternary systems which can be formed from water, two positive, and two negative ions. These systems are:

$$H_2O\text{–}(\overset{+}{Na_2},\overset{+}{K_2})\text{–}(\overset{-}{Cl_2},\overset{-}{SO_4}),$$

$$H_2O\text{–}(\overset{+}{K_2},\overset{+}{Mg})\text{–}(\overset{-}{Cl_2},\overset{-}{SO_4}),$$

and $$H_2O\text{–}(\overset{+}{Na_2},\overset{+}{Mg})\text{–}(\overset{-}{Cl_2},\overset{-}{SO_4}).$$

They are systems formed by water and two reciprocal salt pairs, the type of quaternary system which we discussed in § 70 and the succeeding paragraphs.

The system H_2O–NaCl–KCl–$MgCl_2$[1] is represented at 25°, by Jänecke's method, in Fig. 135. In order to represent the isotherm in a quaternary system of this type within a regular tetrahedron, or its projection within an equilateral triangle, it is not essential to express the compositions of solutions in terms of moles of the components. It is, however, advisable to do so when the isotherm is to be compared with other isotherms in quaternary systems formed by solutions of reciprocal salt pairs, for these isotherms can only be represented within a square when the compositions of solutions

[1] Van't Hoff and Lichenstein, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 235.

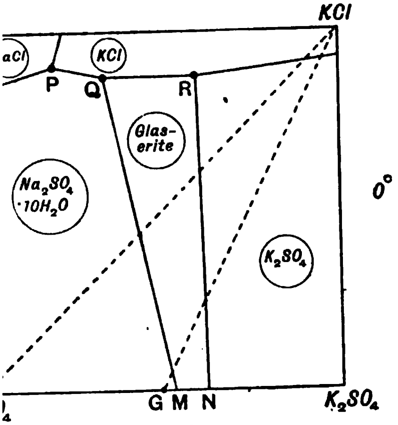

Fig. 136.

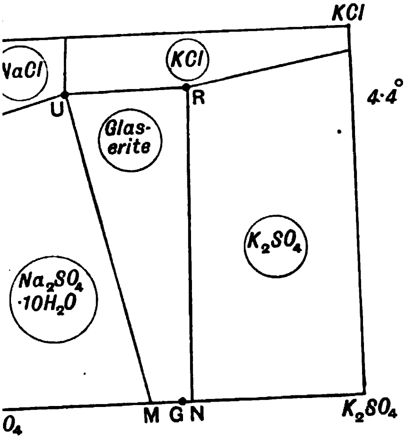

Fig. 138.

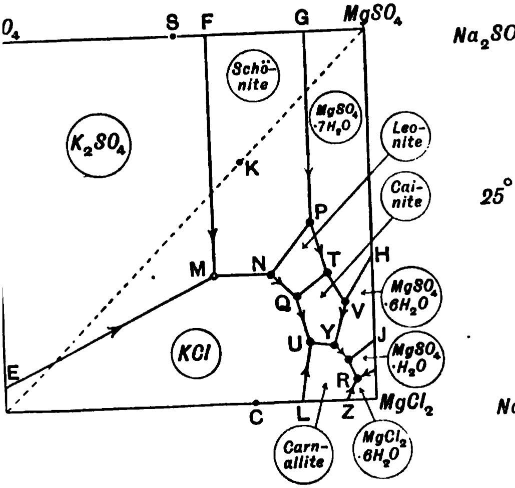

Fig. 141.

SHEET XV

are expressed in terms of moles, or, more strictly, equivalents, of the components (*cf.* § 67).

The system represented in Fig. 135 is comparatively simple, and the isotherm belongs to the type which is illustrated in Fig. 102, and which we have discussed in §§ 63 and 64. The two ternary systems H_2O–$NaCl$–$MgCl_2$ and H_2O–KCl–$NaCl$ are of the simplest type at this temperature, and they each show one isothermal invariant point; the point *A* represents the ternary invariant solution saturated with the two solid phases $NaCl + MgCl_2.6H_2O$, the point *B* that saturated with $KCl + NaCl$.

In the ternary system H_2O–KCl–$MgCl_2$ there occurs, as a solid phase, the hydrated double salt $KCl.MgCl_2.6H_2O$, which is also known as the mineral carnallite. The ternary isotherm shows, therefore, the saturation curve *FG* of carnallite, and the quaternary isotherm shows its saturation surface *FMNG*. The composition of this double salt is represented by the point *C* on the side KCl,$MgCl_2$ of the triangle, and since this point does not lie on the saturation curve of carnallite, it follows that this salt is decomposed by water. The ternary invariant point *G* represents a solution saturated with the two solids KCl + Carnallite, and this solution is incongruently saturated. The quaternary invariant point *N* represents a solution saturated with the three solids KCl + Carnallite + $NaCl$, and, since the point lies outside the triangle KCl, C, $NaCl$, this solution is also incongruently saturated.

The system H_2O–$(\overset{+}{Na_2}, \overset{+}{K_2})$–$(\overset{-}{Cl_2}, \overset{-}{SO_4})$[1] has been thoroughly investigated at several temperatures. The isotherm at 0° is represented, by Jänecke's method, in Fig. 136. Of the ternary systems which form the basis of the quaternary system, the only one which is not of the simplest type at 0° is the system H_2O–Na_2SO_4–K_2SO_4. A double salt, known as Penny's double salt, or as the mineral glaserite, occurs as a solid phase in this system. In composition, it corresponds with the formula $K_3Na(SO_4)_2$, though it forms, to some extent, isomorphous mixtures of varying composition with the simple sulphates Na_2SO_4 and K_2SO_4. The validity of our general conclusions will not, however, be affected if we assume this solid phase to be of constant composition and represented by the above formula; it is given by the point *G* in Fig. 136. The point *M* represents the ternary invariant solution saturated with $Na_2SO_4.10H_2O$ + Glaserite, the point *N* that saturated with K_2SO_4 + Glaserite, and it is clear from the position of the point *G*, outside the saturation curve *MN* of glaserite, that this double salt is decomposed by water, and that the ternary invariant solution *M* is incongruently saturated. In the quaternary isotherm, the saturation surface of $Na_2SO_4.10H_2O$ is separated from that of K_2SO_4 by the saturation surface of glaserite. There are three quaternary isothermal invariant points, and of these the point *R*, since it lies outside the triangle KCl, G, K_2SO_4, and the point *Q*, since it lies outside the triangle KCl, G, Na_2SO_4, represent incongruently saturated solutions; the isotherm cannot, therefore, be divided into simpler parts. The two salts KCl and $Na_2SO_4.10H_2O$ are clearly compatible at this temperature, whilst the salts NaCl and glaserite are incompatible.

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[1] Meyerhoffer and Saunders, *Zeitsch. physikal. Chem.*, 1899, **31**, 380.

The isotherm at 16·3° is represented in Fig. 137, and it is to be seen here that the salt pair KCl + $Na_2SO_4.10H_2O$, which was the stable pair at 0°, is now unstable, whilst the previously incompatible salts NaCl + Glaserite are compatible at this temperature. We have here an example of the change in the stable salt pair, with the temperature, which we discussed in § 74, and we saw that, when such a change occurs, a transition point must exist in the quaternary system at which both salt pairs are in equilibrium with an invariant solution. This transition point has been found to lie, in the present case, at 4·4°, and the isotherm at this temperature is represented in Fig. 138. It can be seen that the four saturation surfaces, the points of which represent solutions saturated with NaCl, with KCl, with glaserite, and with $Na_2SO_4.10H_2O$, all meet in the point *U*. This point gives, therefore, the composition of the solution saturated, at the transition temperature, with NaCl + KCl + Glaserite + $Na_2SO_4.10H_2O$. Below 4·4° the salt pair KCl + $Na_2SO_4.10H_2O$ is the stable pair, as shown in Fig. 136, and above 4·4° the salt pair NaCl + Glaserite is stable, as shown in Figs. 137 and 139. The isothermal relations at 25° are represented in Fig. 139, and these are somewhat more complicated owing to the appearance of anhydrous sodium sulphate as a solid phase. The binary transition point of sodium sulphate decahydrate lies at 32·35°, and this is, therefore, the lowest temperature at which anhydrous sodium sulphate can exist in the binary system H_2O–Na_2SO_4. The ternary transition point of the hydrate, in the system H_2O–Na_2SO_4–$NaCl$, where sodium chloride is present as a third solid phase, lies at 17·9°. At 25°, the saturation curves of both anhydrous sodium sulphate and the decahydrate appear, therefore, in the ternary isotherm, and the saturation surface of the anhydrous salt partially displaces that of the hydrate in the quaternary isotherm. At the transition point of the hydrate in the quaternary system, sodium chloride and glaserite, are present as third and fourth solid phases, in equilibrium with hydrated and anhydrous sodium sulphate and an invariant solution. The corresponding transition temperature is 16·3°, and between this and the ternary transition temperature (17·9°), the saturation surface of anhydrous sodium sulphate must be represented by an entirely enclosed area which surrounds the point *S* of Fig. 137, and which does not extend to the side of the square (*cf.* § 58).

The system H_2O–$(\overset{+}{K_2}, \overset{+}{Mg})$–$(\overset{-}{Cl_2}, \overset{-}{SO_4})$ was studied by Löwenherz[1] at 25°, and this investigator's results are represented, by Jänecke's method, in Fig. 140. Of the four ternary systems which are represented on the sides of the square, two show the saturation curves of hydrated double salts. In the system H_2O–K_2SO_4–$MgSO_4$, the hydrated double sulphate $K_2SO_4.MgSO_4.6H_2O$ occurs as a solid phase; it is known as the mineral schönite, and its composition is represented by the point *S* on the side K_2SO_4,$MgSO_4$ of the square. Since the point *S* lies outside the ternary saturation curve *FG* of schönite, this double salt is decomposed by water, and the solution *F*, which is in equilibrium with the two solid phases K_2SO_4 + Schönite, is incongruently saturated.

In the system H_2O–KCl–$MgCl_2$, the hydrated double chloride, carnallite, occurs as a solid phase; as we have already mentioned, its composition is given by the formula $KCl.MgCl_2.6H_2O$, and it is represented by the point *C* on the side KCl,$MgCl_2$, of the square, in Fig. 140. The point *C* lies outside the ternary saturation curve *LZ*, of carnallite, and this salt is, therefore, also decomposed by water, the solution *L*, which is in equilibrium with the two solid phases KCl + Carnallite, being also incongruently saturated.

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[1] *Zeitsch. physikal. Chem.*, **1894, 13, 459.**

In the ternary system H_2O–$MgSO_4$–$MgCl_2$, the heptahydrate $MgSO_4.7H_2O$, which is the stable solid phase at 25°, in the binary system H_2O–$MgSO_4$, suffers dehydration at a certain concentration of magnesium chloride, and the ternary isotherm contains the saturation curves of both hepta- and hexa-hydrate.

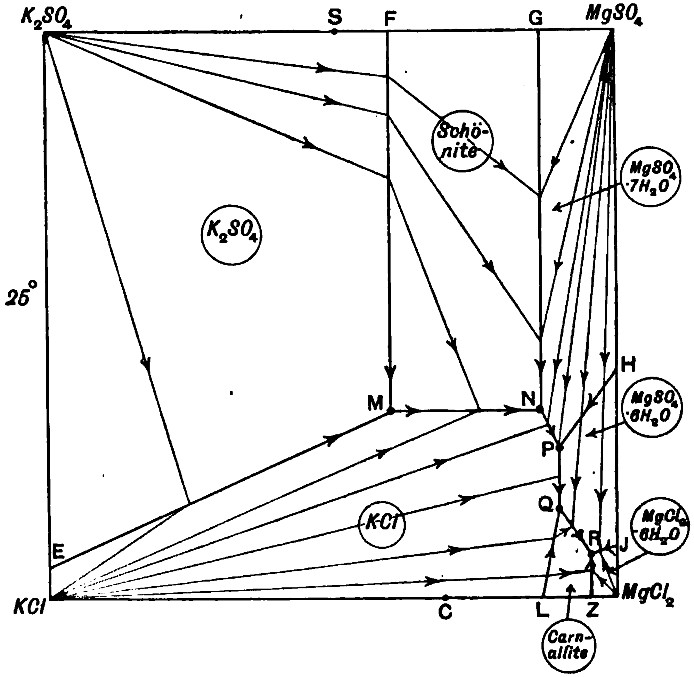


FIG. 140.

There are, therefore, two invariant points in this ternary system; the point *H* represents the solution which is in equilibrium with $MgSO_4.7H_2O$ + $MgSO_4.6H_2O$, and the point *J* that in equilibrium with $MgSO_4.6H_2O$ + $MgCl_2.6H_2O$.

The ternary system H_2O–K_2SO_4–KCl is of the simplest type, and it shows the single invariant point *E*, which represents a solution in equilibrium with the two solid salts K_2SO_4 and KCl.

Seven saturation surfaces occur, therefore, in the quaternary isotherm, namely, those of two double salts and one salt hydrate besides the four saturation surfaces of the simple salts or their stable hydrates in the binary systems. It can be seen that the two salts $MgSO_4$ and KCl form the stable pair, though in regions which represent solutions of comparatively high potassium sulphate content the saturation surface of magnesium sulphate is displaced by that of the double sulphate, and in regions which represent solution of comparatively high magnesium chloride content, the saturation surface of potassium chloride is displaced by that of the double chloride. It will be found on examination that, of the five quaternary invariant solutions *M*, *N*, *P*, *Q*, and *R*, the first four are incongruently saturated, like the ternary invariant solutions *F* and *L*. The point *R* represents the only congruently saturated, quaternary invariant solution, and it is therefore the drying-up point of all quaternary solutions, if the solid phases are removed as fast as they separate. The paths of crystallisation on the saturation surfaces are marked in Fig. 140. Those on the schönite saturation surface radiate from the point *S*, which represents a metastable solution saturated with schönite, and containing only schönite; such a solution would, actually, be supersaturated with potassium sulphate. In the same way, the paths of crystallisation on the saturation surface of carnallite radiate from the point *C*, which represents the metastable solution containing only carnallite, and saturated with that salt; this solution is supersaturated with potassium chloride.

The isotherm shown in Fig. 140 is based upon the results of Löwenherz, but the later work of van't Hoff has shown that some of the solutions represented by points in this isotherm are in a state of metastable equilibrium.

The existence of the hydrated double salt schönite ($K_2SO_4.MgSO_4.6H_2O$) is limited to a certain temperature range. At − 3° it possesses a transition point which marks a *lower* stability limit to its existence in the ternary system H_2O–$MgSO_4$–K_2SO_4; at this transition point the double salt is in equilibrium with the two simple salts $MgSO_4.7H_2O$ and K_2SO_4, and a ternary invariant solution. The range of existence of this compound is also limited, however, on the side of higher temperatures, for, in the presence of a third solid phase, it suffers partial dehydration at a second definite transition temperature, and a lower hydrate is formed which is known as leonite, and which corresponds with the formula $K_2SO_4.MgSO_4.4H_2O$.

The temperature at which the dehydration of schönite occurs, in the presence of $MgSO_4.7H_2O$ as a third solid phase, is 41°. At this ternary transition point the three solid phases schönite, leonite, and $MgSO_4.7H_2O$ are all in equilibrium with an invariant solution; above 41° leonite can occur as a solid phase in the system H_2O–$MgSO_4$–K_2SO_4, and its saturation curve must then appear in the ternary isotherm. The transition temperature of schönite to leonite is lowered by the presence of a fourth component, in exactly the same way as is the transition temperature of a hydrated simple salt. The transition point of schönite to leonite, in the quaternary system H_2O–$(\overset{+}{K_2}, \overset{+}{Mg})$–$(\overset{-}{Cl_2}, \overset{-}{SO_4})$, occurs at 20° in the presence of KCl and $MgSO_4.7H_2O$ as third and fourth solid phases. It is clear, therefore, that the saturation surface of leonite must appear in the quaternary isotherm above 20°. The temperature of the isotherm shown in Fig. 140 (25°) lies between the quaternary and the ternary transition points of schönite, and the saturation surface of leonite must, therefore, appear in the isotherm as an enclosed area which does not extend into the side K_2SO_4,$MgSO_4$ of the square. A part of the saturation surface of schönite, as given in the isotherm of Fig. 140, must, in other words, represent solutions supersaturated with respect to leonite. This body possesses the property of easily forming supersaturated solutions, which deposit solid leonite only in the presence of a crystal of this salt, and it was for this reason that Löwenherz failed to recognise its possible existence as a stable solid phase in the quaternary system at 25°.

We have seen that, according to the isotherm of Fig. 140, the reciprocal salt pair KCl + $MgSO_4$ aq., can exist in equilibrium with solutions the compositions of which are represented by points on the saturation curves *NP* and *PQ*. Subsequent work has shown that these solutions are also metastable, being supersaturated with respect to a compound of the two salts; the composition of this compound is represented by the formula $KCl.MgSO_4.3H_2O$, and it is known as the mineral cainite. If the system H_2O–KCl–$MgSO_4$ were a ternary system, cainite would be a ternary compound. The line KCl, $MgSO_4$ of Fig. 140 intersects, however, besides the saturation surfaces of KCl and $MgSO_4.7H_2O$, those of K_2SO_4 and schönite. The system is, therefore, quaternary and not ternary, and cainite is a quaternary compound and not, as it appears at first sight, a ternary compound. It will be seen that the composition of cainite, which corresponds with the formula $KCl.MgSO_4.3H_2O$, can equally well be represented by the formula $K_2SO_4.MgSO_4.MgCl_2.6H_2O$. Cainite can be considered, therefore, as a hydrated triple salt, and it may be compared with the quaternary compound $NaNO_3.CaS_2O_3.$ $.Na_2S_2O_3.11H_2O$, which we discussed earlier in this paragraph. The composition of cainite, since it can be expressed in terms of a reciprocal salt pair only, must be represented by a point on a diagonal of the square (the diagonal KCl, $MgSO_4$), whilst that of the hydrated triple salt in the system $H_2O–(\overset{+}{Na_2}, \overset{+}{Ca})–$ $(\overset{-}{S_2O_3},)\ [\overset{-}{NO_3}]_2)$ cannot be so expressed, and is not, therefore, represented by a point on a diagonal of the square; since the diagonal $KCl,MgSO_4$ does not represent the isotherm in a ternary system, cainite is, nevertheless, a quaternary compound. A compound, such as cainite, the composition of which can be expressed in terms of water and one of the reciprocal pairs alone, has been called by Meyerhoffer a "tetragenic double salt." If the system formed by water and the reciprocal salt pair is ternary, the tetragenic double salt is to be considered as a ternary compound; if this system is quaternary, then the tetragenic double salt must be considered as a quaternary compound. The conditions of *stable* equilibrium in the system

$$H_2O–(\overset{+}{K_2}, \overset{+}{Mg})–(\overset{-}{Cl_2}, \overset{-}{SO_4})$$

at 25° are represented diagrammatically in Fig. 141; this figure shows the saturation surfaces of leonite and cainite, which replace the metastable areas in Fig. 140. The composition of cainite is represented by the point *K*, which lies on the diagonal KCl, $MgSO_4$ of the square. Since this point falls on the saturation surface of schönite, it follows that an unsaturated solution formed by dissolving cainite in water must first deposit schönite on the evaporation of water, and the point representing the composition of the solution, as the evaporation proceeds, will follow a path of crystallisation on the schönite saturation surface. The solution will ultimately dry, like all other quaternary solutions, at the constant composition of the final drying-up point *R*, provided that the solid phases are removed from contact with the liquid; it is clear that the system H_2O–Cainite is a quaternary system.

The fact that cainite is decomposed by water with the separation of schönite ($K_2SO_4.MgSO_4.6H_2O$) suggests the formula $K_2SO_4.MgSO_4.MgCl_2.6H_2O$ for cainite, rather than the simpler formula $KCl.MgSO_4.3H_2O$. On the other hand, we can consider cainite and carnallite as being formed from one another, at a quaternary system invariant point, by the following reactions:

$$\underset{\text{Cainite}}{KCl,MgSO_4aq.} + MgCl_2aq. \rightleftarrows \underset{\text{Carnallite.}}{KCl.MgCl_2aq.} + MgSO_4aq.$$

We see that cainite, magnesium chloride, carnallite, and magnesium sulphate, are related one to another, in the same way as are the four salts of the reciprocal salt pairs $(\overset{+}{A}, \overset{+}{C})$–$(\overset{-}{B}, \overset{-}{D})$. It appears from Fig. 141 that the two salts cainite and magnesium chloride are incompatible at 25°, whilst carnallite and magnesium sulphate form the stable pair; solutions saturated with this stable salt pair are represented by points on the saturation curves *UYR*. It is possible that, at some quaternary transition temperature, all four salts may be capable of existing in equilibrium with one another, as represented by the scheme given above.

Finally, we may mention that some of the solutions represented by points on the saturation surface of $MgSO_4.6H_2O$ in the isotherm of Löwenherz (Fig. 140) were found to be supersaturated with respect to the lower hydrate $MgSO_4.H_2O$. This hydrate, which occurs as the mineral kieserite, forms supersaturated solutions which pass very slowly into the stable phase complexes, even in the presence of a crystal of the stable solid phase. The saturation surface of $MgSO_4.H_2O$ is shown in the isotherm of Fig. 141.

As a last example, the isotherm at 25°, in the system H_2O–$(\overset{+}{Na_2}, \overset{+}{Mg})$–$(\overset{-}{Cl_2}, \overset{-}{SO_4})$, is represented diagrammatically in Fig. 142. This system differs from the one which we have just discussed in the fact that the potassium ion is here replaced by the sodium ion. The isotherm in the ternary system H_2O–$MgSO_4$–$MgCl_2$ at 25° is represented on the side $MgSO_4$,$MgCl_2$ of the square in both the figures 141 and 142. The saturation surfaces which are bounded by this side must, therefore, be identical in the two quaternary isotherms; they are the saturation surfaces of the three hydrated magnesium sulphates and of magnesium chloride hexahydrate. There appears as a solid phase in the ternary system H_2O–Na_2SO_4–$MgSO_4$, the hydrated double salt astrakanite. This double salt is isomorphous with leonite, which occurs as a solid phase in the system H_2O–K_2SO_4–$MgSO_4$; its composition is represented by the formula $Na_2SO_4.MgSO_4.4H_2O$, which is similar to that of leonite, the potassium in the latter compound being here replaced by sodium. The sodium analogue of the more highly hydrated potassium magnesium sulphate, schönite, does not occur. The ternary system H_2O–$NaCl$–$MgCl_2$ is of the simplest type, and no double salt analogous to carnallite appears. The ternary system H_2O–$NaCl_2$–Na_2SO_4 shows the isothermal saturation curves of both the hydrated and anhydrous sulphate $Na_2SO_4.10H_2O$ and Na_2SO_4.

The quaternary isotherm is much simpler than that in the system $H_2O–(\overset{+}{K_2}, \overset{+}{Mg})–(\overset{-}{Cl_2}, \overset{-}{SO_4})$ at the same temperature. The two salts NaCl and $MgSO_4$ aq. form the stable salt pair, and solutions saturated with these salts are represented by points on the curves *CD*, *DE*, *EF*. No tetragenic double salt analogous to cainite occurs in this system, and the hydrated double sulphate, astrakanite, does not suffer dehydration in the quaternary system at 25°.

CHAPTER IV

CONDENSED QUINARY SYSTEMS

§ 77. HITHERTO, we have always chosen water and certain of the salts as independent components of a system formed by aqueous salt solutions. This is, however, a matter of convenience, and there exists no reason why we should not choose water and certain of the ions as independent components, as we have already pointed out in § 3. The system formed by water and the two salts *AC* and *BC*, which have an ion in common, is a ternary system, and, as independent components, we have chosen water and the two salts themselves. If we choose water and the ions as components, it is clear that we cannot consider all three ions, $\overset{+}{A}$, $\overset{+}{B}$, and $\overset{-}{C}$, as independent components, since the system is not quaternary. The absolute amounts of the three ions, in any phase, are related to one another by the fact that the sum of the positive ions, expressed in equivalents, is equal to the sum of the negative ions similarly expressed. The amount of one ion in any phase is determined when the amounts of the other two are given, and only two of the ions can be considered, therefore, as independent components. In general, we can say that a system which is formed by water and n different ions is a system of the nth order; water and $n - 1$ of the n ions can be considered as the n independent components of the system. Thus, a quaternary system is formed by water and four different ions, of which three may be considered as independent components; of the four ions, three may be of the same sign, or two may be of one sign and two of the other. We thus obtain the two different types of quaternary system which were discussed in the previous chapter, namely, the type illustrated by

$$W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{-}\overset{-}{D}$$

or

$$W\text{-}AD\text{-}BD\text{-}CD,$$

which is formed by water and three salts having a common ion, and the type illustrated by

$$W\text{-}(\overset{+}{A}, \overset{+}{C})\text{-}(\overset{-}{B}, \overset{-}{D}),$$

which is formed by water and two reciprocal pairs.

A system of five components is formed by water and five different ions, four of which may be considered as independent components; here again, there exist two possibilities, for, of the five ions, four may be of like sign, or three may be of one sign and two of the other. We must consider, therefore, the two following types of quinary system:

$$\begin{array}{ll} & \left.\begin{array}{l} W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C}, \overset{+}{D})\text{-}\overset{-}{E}\ . \\ W\text{-}AE\text{-}BE\text{-}CE\text{-}DE \end{array}\right\} . \quad . \quad . \quad . \quad . \quad 1. \\ \text{or} & \end{array}$$

and

$$\begin{array}{ll} & \left.\begin{array}{l} W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E}) \\ W\text{-}AD\text{-}BD\text{-}CD\text{-}AE\text{-}BE\text{-}CE \end{array}\right\} . \quad . \quad 2. \\ \text{or} & \end{array}$$

It follows from the phase rule that when six phases are in equilibrium in the condensed system of five components, at constant pressure, then the equilibrium is invariant; five solid phases in equilibrium with a solution will occur, therefore, at a quinary system invariant point. Five phases in equilibrium with one another constitute a monovariant quinary system at constant pressure, and four solid phases will occur, therefore, in equilibrium with a solution at an isothermal invariant point. The isothermal saturation curves will represent solutions in equilibrium with three solid phases, and the isothermal saturation surfaces solutions in equilibrium with two solid phases.

§ 78. It is clear that the difficulty of obtaining a graphical representation of the equilibrium conditions increases as the number of independent components in the system increases. Thus, in the condensed binary system, we were able to obtain a complete polythermal representation in one plane, *i.e.*, a complete representation of the relations which exist, at constant pressure, between temperature and the compositions of solutions. In the condensed ternary system a space figure was necessary for this purpose; the isothermal conditions of equilibrium could alone be represented completely in one plane. In the condensed quaternary system the complete polythermal conditions of equilibrium could no longer receive complete graphical expression, and the isothermal relations could be completely represented only by means of a space figure. In the quinary system it is not possible to obtain a complete representation, even of the isothermal conditions of equilibrium, in one space figure.

We will first suppose that the quinary system is formed by water and four salts with a common ion (type 1 of § 77); we will denote the salts, briefly, by the symbols S_1, S_2, S_3, and S_4, and we will choose water and these four salts as independent components of the system. We will express the compositions of solutions in Jänecke's form:

$$mW,xS_1,yS_2,zS_3,(100-\overline{x+y+z})S_4 \quad . \quad . \quad 1.$$

where the sum of the concentrations of the four salts is equal to 100. The concentration variable m, which gives the water content of solutions, will then be considered independently from the variables x, y, and z, which give the percentage compositions of the salt mixtures contained by solutions (*cf.* § 56). Now in the quinary polytherm we must have, as independent variables, the temperature T, the water content m of the solutions, and the three factors x, y, and z, which give the compositions of salt mixtures. In order to represent the simultaneous variations of these five independent variables we should require a figure in five dimensions. If the temperature T is considered constant, then the simultaneous variations of the four factors m, x, y, and z would represent the isothermal behaviour of the system; but this variation would still require a figure in four dimensions for complete graphical expression. If, however, we choose to leave the water content m, of solutions, unexpressed, then we can obtain a partial representation of the quinary isotherm by means of a figure in three dimensions, a representation which shows the simultaneous variations of the three factors x, y and z. This figure will give only the compositions of the salt mixtures contained in solutions saturated at a fixed temperature, and it will not give the total

Fig. [illegible]

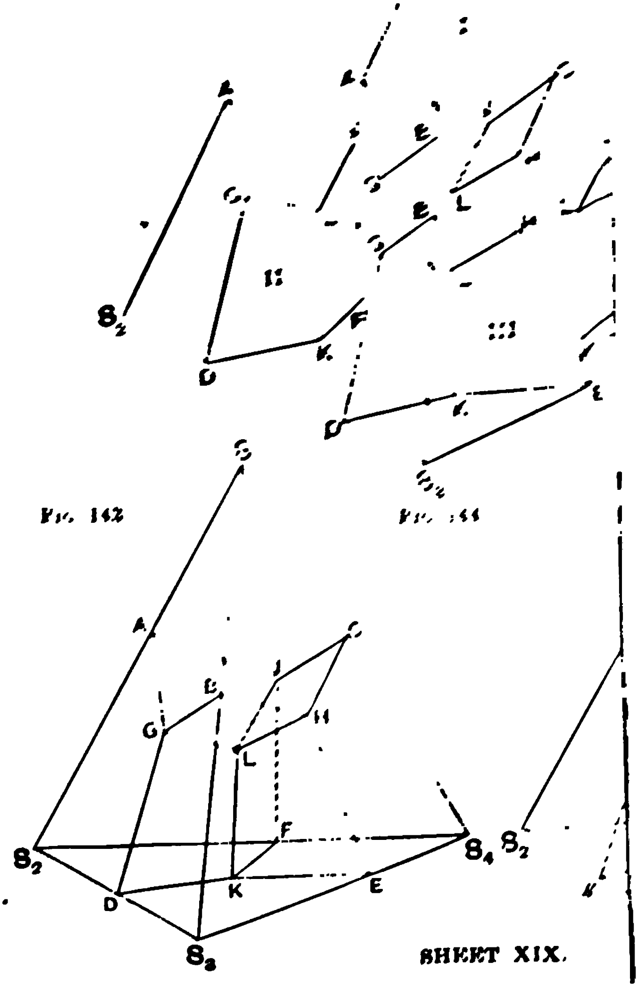


Fig. 142

Fig. 144

SHEET XIX.

mpositions of such solutions; to every point in the figure ere will correspond an unexpressed, though definite, value or the water content m, and this value will vary from point o point. If the positions of points in the space figure are referred to the faces of a regular tetrahedron, as described in § 49, it will be possible to give actual graphical expression, not only to the independent variables x, y, and z, but also to the dependent variable $100 - \overline{x + y + z}$, which occurs in the form 1 of this paragraph, and which gives the concentration of the fourth salt in the salt mixture. This will be clear from § 49 without further explanation.

§ 79. The isotherm in the system W–S_1–S_2–S_3–S_4, when only the component salts occur as solid phases, is represented by Jänecke's method in Fig. 143. The four corners of the regular tetrahedron $S_1S_2S_3S_4$ represent the four pure salts, and a point within the tetrahedron represents the percentage composition of the salt mixture contained by a saturated solution, in such a way that the distance of the point from the face opposite to the S_1 corner gives the percentage of S_1 contained in the mixture, its distance from the face opposite to the S_2 corner gives the percentage of S_2 etc.; if the edge of the tetrahedron measures 100, then these distances must be measured parallel to the edges of the tetrahedron as described in § 49, and their sum will be equal to the length of an edge, *i.e.*, to 100. As the basis of this quinary system, we must consider the four quaternary systems W–S_1–S_2–S_3, W–S_1–S_3–S_4, W–S_1–S_4–S_2, and W–S_2–S_3–S_4, and the isotherms in these systems are represented one in each of the faces of the tetrahedron. The isotherm in the quaternary system W–S_1–S_2–S_3 is represented, for example, by Jänecke's method, in the face $S_1S_2S_3$, and it is to be compared with the simple quaternary type which was illustrated in Fig. 82. The point G represents the quaternary invariant solution saturated, at the temperature of the isotherm, with the three salts $S_1 + S_2 + S_3$. Points on the curve GL, which, starting from the point G, extends into the interior of the tetrahedron, represent quinary solutions which are also saturated with these three salts. It is the quinary saturation curve of $S_1 + S_2 + S_3$, and it ends in the quinary invariant point L, which represents the solution saturated, at the temperature of the isotherm, with the

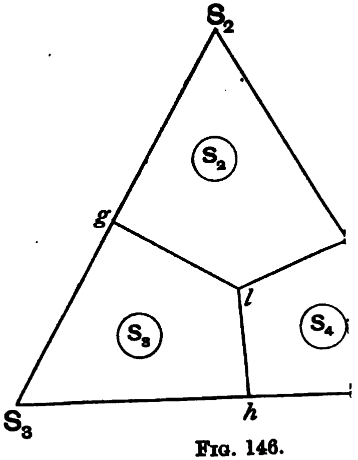


FIG. 146.

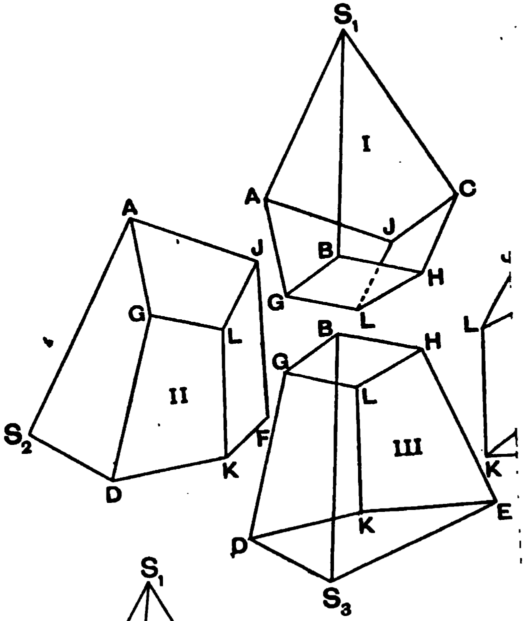


FIG. 144.

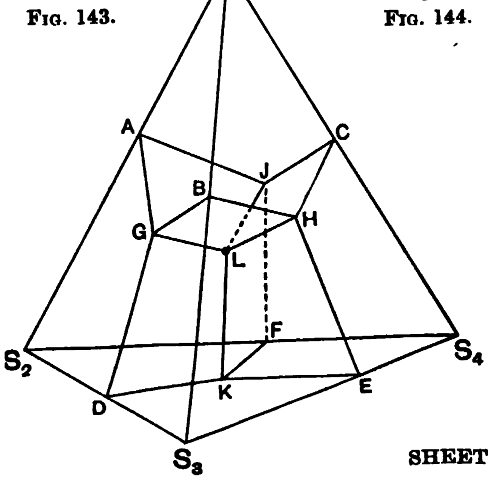
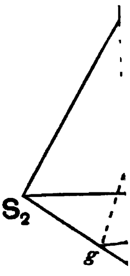


FIG. 143.



SHEET XIX.

compositions of such solutions; to every point in the figure there will correspond an unexpressed, though definite, value for the water content m, and this value will vary from point to point. If the positions of points in the space figure are referred to the faces of a regular tetrahedron, as described in § 49, it will be possible to give actual graphical expression, not only to the independent variables x, y, and z, but also to the dependent variable $100 - \overline{x + y + z}$, which occurs in the form 1 of this paragraph, and which gives the concentration of the fourth salt in the salt mixture. This will be clear from § 49 without further explanation.

§ 79. The isotherm in the system W–S_1–S_2–S_3–S_4, when only the component salts occur as solid phases, is represented by Jänecke's method in Fig. 143. The four corners of the regular tetrahedron $S_1S_2S_3S_4$ represent the four pure salts, and a point within the tetrahedron represents the percentage composition of the salt mixture contained by a saturated solution, in such a way that the distance of the point from the face opposite to the S_1 corner gives the percentage of S_1 contained in the mixture, its distance from the face opposite to the S_2 corner gives the percentage of S_2 etc.; if the edge of the tetrahedron measures 100, then these distances must be measured parallel to the edges of the tetrahedron as described in § 49, and their sum will be equal to the length of an edge, *i.e.*, to 100. As the basis of this quinary system, we must consider the four quaternary systems W–S_1–S_2–S_3, W–S_1–S_3–S_4, W–S_1–S_4–S_2, and W–S_2–S_3–S_4, and the isotherms in these systems are represented one in each of the faces of the tetrahedron. The isotherm in the quaternary system W–S_1–S_2–S_3 is represented, for example, by Jänecke's method, in the face $S_1S_2S_3$, and it is to be compared with the simple quaternary type which was illustrated in Fig. 82. The point G represents the quaternary invariant solution saturated, at the temperature of the isotherm, with the three salts $S_1 + S_2 + S_3$. Points on the curve GL, which, starting from the point G, extends into the interior of the tetrahedron, represent quinary solutions which are also saturated with these three salts. It is the quinary saturation curve of $S_1 + S_2 + S_3$, and it ends in the quinary invariant point L, which represents the solution saturated, at the temperature of the isotherm, with the four salts $S_1 + S_2 + S_3 + S_4$. We have already shown in § 77 that the isothermal invariant point in the five component system represents a solution which is in equilibrium with four solid phases, and that points on the isothermal saturation curves represent solutions which are in equilibrium with three solid phases.

It can be seen that the remaining quaternary isotherms, which are represented on the other three faces of the tetrahedron in Fig. 143, are also of the simplest type, and that each quaternary invariant point forms the starting point of a quinary saturation curve which ends in the quinary invariant point *L*.

The surface *AGLJ* is bounded in the faces $S_1S_2S_3$ and $S_1S_2S_4$ by the curves *AG* and *AJ*, which are the saturation curves of $S_1 + S_2$ in the two quaternary systems which contain both these salts. This surface is, therefore, the quinary saturation surface of $S_1 + S_2$. There are five other quinary saturation surfaces in the isotherm, namely, *BGLH* that of $S_1 + S_3$, *CHLJ* that of $S_1 + S_4$, *DGLK* that of $S_2 + S_3$, *FJLK* that of $S_2 + S_4$, and *EHLK* that of $S_3 + S_4$.

The saturation surfaces divide the interior of the tetrahedron into four spaces, the points of which represent solutions saturated with one salt; these spaces can be distinguished more clearly in Fig. 144, where they are shown separated from each other. The space I in this figure is bounded, in the faces $S_1S_2S_3$, $S_1S_3S_4$, and $S_1S_4S_2$, by the surfaces S_1AGB, S_1BHC, and S_1CJA, which are the saturation surfaces of S_1 in the three quaternary systems which contain this salt; this space is, therefore, the quinary saturation space of S_1. The space II is, similarly, the saturation space of S_2, the space III that of S_3, and the space IV that of S_4.

It may be mentioned that the quinary phase complexes and unsaturated solutions can no longer be represented; this arises from the fact that the representation of the quinary isotherm is necessarily incomplete. A point within the tetrahedron of Fig. 143 defines a salt mixture of a certain composition, and, if this salt mixture is contained by a saturated solution, the water content will also possess a definite value corresponding with, though not expressed by, the point. If we do not make this assumption then the point may represent, at one and the same time, either an unsaturated solution (if the water content is greater than corresponds with a saturated solution), or a phase complex (if the water content is less than that of the saturated solution). We see, therefore, that a definite meaning can be attached to a point within the tetrahedron of Fig. 143 only if we assume it to represent a saturated solution; only in this case will there correspond, with each point in the figure, a definite value for the water content, and, unless this assumption is made, a given point may represent, at one and the same time, a saturated solution, an unsaturated solution, and a phase complex. These conclusions are true of any graphical representation which, while giving the compositions of salt mixtures, omits to give expression to the water content—the representation is free from ambiguity only if all points are assumed to denote saturated solutions; they apply, for example, to Jänecke's plane representation of the ternary polytherm (§ 38), and to Jänecke's plane representation of the quaternary isotherm (§ 56).

A representation of the quinary isotherm in one plane can be obtained by a projection of the space figure; we may, for example, project the figure upon the base of the tetrahedron. Since, however, the base of the tetrahedron already contains the quaternary isotherm in the system $W–S_2–S_3–S_4$, it is better to project each saturation space separately, upon the tetrahedral face which is opposite to it. In Fig. 145 there is shown a part only of the quinary isotherm, namely, the quinary saturation space $S_1AGBHCJL$, of the salt S_1, with its boundary surfaces and curves (*cf.* Figs. 143 and 144). This space is bounded, namely, by three quinary saturation surfaces, the points of which represent solutions saturated, not only with S_1, but also with one other salt S_2, S_3, or S_4. These surfaces, intersecting by pairs, form three quinary saturation curves the points of which represent solutions saturated, not only with S_1, but also with two other salts, and the saturation curves intersect in a point which represents a solution saturated, not only with S_1, but also with all three other salts. We will now suppose that the saturation space of S_1 is projected upon the face $S_2S_3S_4$ of the tetrahedron, by means of lines which radiate from the point S_1, as shown by the dotted lines in Fig. 145, and in exactly the same way as the quaternary isotherm was projected in § 56. The projection is shown on the base on the tetrahedron in Fig. 145, and in the plane of the paper in Fig. 146. Since Fig. 146 is the projection of the quinary saturation space of S_1, *every point* in it must represent a solution saturated with this salt, but, here again, a certain assumption must be made if the points of this figure are to have definite meanings. The point K (Fig. 145) lies, for example, on the saturation surface of $S_1 + S_2$, and it represents a solution which is saturated with these two salts, and which has a definite, though unexpressed, water content; its projection on the base of the tetrahedron is given by the point k, but it is clear that this point k is also the projection of all points on the line S_1K, which, since they lie in the saturation space of S_1, represent solutions, of varying water content, all saturated with the single salt S_1. The point k will, therefore, only possess a definite meaning if we assume that it represents a solution saturated, not with the salt S_1 alone, but also with the second solid phase S_2. Similar considerations can be applied to all points in Fig. 146; they will acquire a definite meaning only if they are assumed to represent solutions saturated, not alone with S_1, but also with at least one other solid phase. Thus points in the area S_2glj must be considered only as the projections of points on the saturation surface $AGLJ$, of $S_1 + S_2$; as it is already understood that *all* points in Fig 146 represent solutions saturated with S_1, it is only necessary to indicate, in the figure, the second solid phase with which solutions are saturated, and the surface S_2glj is, therefore, marked with the solid phase S_2 only. In the same way, points on the surface S_3glh of Fig. 146, if they are to acquire a definite meaning, must be considered only as the projections of points on the saturation surface $BGLH$, of $S_1 + S_3$ (Fig. 145), and the surface S_3glh is therefore marked with the solid phase S_3. Points on the curve gl (Fig. 146) then represent solutions saturated, not only with the two salts $S_2 + S_3$, but also with the salt S_1; similar considerations may be applied to the saturation surface marked S_4 and to the two remaining saturation curves jl and hl—their points represent solutions saturated with S_1, and with the additional solid phase, or solid phases, indicated in the figure. We may say that Fig. 146 gives an (incomplete) representation of the equilibrium in the system W–S_1–S_2–S_3 when it is restricted by the following conditions: 1, the temperature is constant, and 2, the salt S_1 is *always* present as a solid phase in equilibrium with other solid phases and a solution.

The saturation space of the salt S_2 can be projected, in a similar way, upon the face $S_1S_3S_4$ of the tetrahedron, that of the salt S_3 upon the face $S_1S_2S_4$, and that of the salt S_4 upon the face $S_1S_2S_3$. Any one of the plane figures obtained in this way will naturally give a very incomplete quantitative representation of the conditions of equilibrium. Thus a point in Fig. 146 gives only the concentrations of the three salts S_2, S_3, and S_4 contained by a saturated solution, these concentrations being expressed as percentages of the total weight of the three salts $S_2 + S_3 + S_4$ which is present in the solution. Like the points in the space figure (Fig. 145), the points of the projection (Fig. 146) leave the water content of solutions unexpressed, and, in addition, the concentration of the salt S_1, with which every solution is saturated, receives no expression in the projection; to every point in such a projection, there correspond definite, though unexpressed, values for two concentration factors—those of water and of S_1.

It can be seen that the projection, given in Fig. 146, of the saturation space of S_1 in the quinary isotherm

$$W\text{–}S_1\text{–}S_2\text{–}S_3\text{–}S_4,$$

is identical *in form* with the quaternary isotherm

$$W\text{–}S_2\text{–}S_3\text{–}S_4,$$

as shown, for example, on the base of the tetrahedron in Fig. 143. To a given saturation surface, the points of which represent solutions saturated with a certain salt in the quaternary system W–S_2–S_3–S_4, there corresponds a similar surface in the projection of the quinary saturation space —a surface the points of which represent solutions saturated with that same salt plus S_1; to a given saturation curve, the points of which represent solutions saturated with a certain salt pair in the quaternary system, there corresponds a similar curve in the quinary projection—a curve the points of which represent solutions saturated with that same pair plus S_1.

The projection of the saturation space of S_1 in the quinary system would still be of the same form as the isotherm in the quaternary system W–S_2–S_3–S_4 even though the latter, instead of possessing the simple form which we have assumed for it, showed the saturation surfaces of binary or ternary compounds; to the saturation surface of a compound in the quaternary system there would correspond a saturation surface of the compound plus S_1 in the quinary projection. This would no longer be true, however, if the salt S_1 itself formed compounds with any of the other salts. If, for example, the salt S_1 formed a binary compound $S_1.S_2$ with the salt S_2, then the quinary saturation space of S_1 would be bounded partly by the saturation surface of $S_1 + S_1.S_2$. The compound $S_1.S_2$ could not occur, however, in the quaternary system W-S_2–S_3–S_4, and the quaternary isotherm could not contain a corresponding saturation surface.

§ 80. We will consider next the graphical representation of quinary mixtures in systems formed by water and five ions, three of which are of one sign and two of the other (type 2, § 77). In the system

$$W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E}),$$

the following six salts can occur as solid phases:

$$AD, BD, CD, AE, BE, CE.$$

Since, as we have shown, the system is one of five components, we can only consider four of these salts as independent components. In order to avoid an arbitrary choice of salts, we shall express the compositions of solutions in terms of the ions, as we did in the case of quaternary phases formed by solutions of reciprocal salt pairs (§ 73); here, again, we shall express the concentrations of the positive ions in equivalents in such a way that their sum, and therefore also the sum of the concentrations of the negative ions similarly expressed, is equal to 100. The composition of the liquid phase will, therefore, be expressed in the following mathematical form:

$$mW, x\overset{+}{A}, y\overset{+}{B}, (100 - \overline{x + y})\overset{+}{C}, z\overset{-}{D}, (\overline{100 - z})\overset{-}{E} \quad . \quad 1.$$

An examination of this form will show that the concentration variables which are used to define the composition of quinary solutions can be divided into three groups. The first group contains only the variable m, which gives the water content of the solution. The second group contains the two independent variables x and y, and the dependent variable $100 - \overline{x + y}$. These give the percentage composition of the mixture of positive ions contained by the solution; among 100 equivalents of the positive ions, there are x equivalents of the ion $\overset{+}{A}$, y equivalents of the ion $\overset{+}{B}$, and the remaining $100 - \overline{x + y}$ equivalents are formed by the third positive ion $\overset{+}{C}$. The third group of concentration variables contains the independent variable z, and the dependent variable $\overline{100 - z}$. These give the percentage composition of the mixture of negative ions contained by the solution; among 100 equivalents of the total negative ions there are z equivalents of the ion $\overset{-}{D}$, the remaining $\overline{100 - z}$ equivalents being formed by the ion $\overset{-}{E}$. We have assumed here that the three ions A, B, and C are all positive, but a similar treatment can clearly be applied to the case of salt mixtures which contain three negative and two positive ions.

We can represent in space the simultaneous variations of the three independent variables x, y, and z of the form 1, but, in this case, we must leave the water content of solutions (m) unexpressed. We see again that it is only possible to represent, in a space figure, the compositions of the salt mixtures contained by quinary solutions; since we are limited to three dimensions the representation of the quinary isotherm is, at the best, a partial representation.

By means of the following method, which is due to Jänecke, we are able to give graphical expression, not only to the three independent variables x, y, and z of the form 1, but also to the two dependent variables $100 - \overline{x + y}$ and $100 - z$. Fig. 147 represents a prism the triangular faces of which, AD, BD, CD, and AE, BE, CE, are equilateral, and the quadrilateral faces of which, AD, AE, BE, BD; AD, AE, CE, CD; and BD, BE, CE, CD, are square. The eight edges of the prism are, therefore, equal to one another in length, and this length is chosen to represent 100. Every point in the triangular face AD, BD, CD represents the composition of a salt mixture which contains the single negative ion $\bar{D}$; such salt mixtures can be considered as the limiting cases of mixtures that contain both negative ions, namely, the limiting case in which the concentration of the ion E has become equal to zero; the percentage composition of the "mixture" of negative ions is

$$100\bar{D},\ 0\bar{E},$$

Every point in the triangular face *AE*, *BE*, *CE* represents the composition of a salt mixture that contains the single negative ion $\bar{E}$, and such salt mixtures must again be considered as

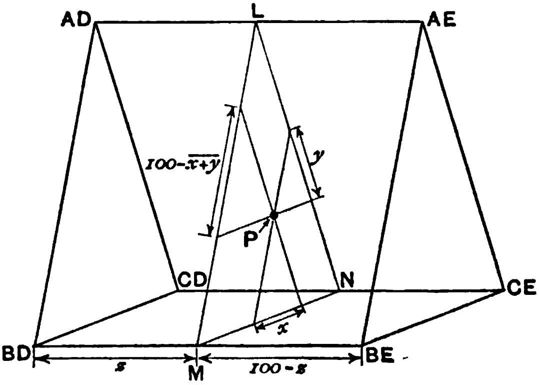


FIG. 147.

limiting cases; the percentage composition of the "mixture" of negative ions is here

$$0\bar{D},\ 100\bar{E}.$$

Points in a section *LMN* of the prism, parallel to the triangular faces, represent salt mixtures which contain both negative ions $\bar{D}$ and $\bar{E}$, but which all contain these two in the same proportion. Of the total negative ions, the percentage of the ion $\bar{D}$ which is contained in these mixtures is measured by the distance of the section from the end face *AE*, *BE*, *CE*, the points of which represent salt mixtures containing none of this ion. It is given, therefore, by either of the lengths *L*, *AE*; *M*, *BE*; or *N*, *CE*, which we will call z in accordance with the mathematical form 1. The percentage of the ion $\bar{E}$ on the total negative ions is $100 - z$, and, since we have chosen the edge of the prism to represent 100, this percentage is given by either of the lengths L, AD; M, BD; or N, CD. It is given by the distance of the section from the end face AD, BD, CD, the points of which represent salt mixtures containing none of the ion $\bar{E}$. We can say, therefore, that all points in the section LMN represent salt mixtures containing the two negative ions $\bar{D}$ and $\bar{E}$ in the proportion

$$z\bar{D}, \overline{100 - z}\bar{E}.$$

We have thus limited the position of the point that represents a salt mixture of a given composition to a certain plane section of the space figure. The precise position of the point in this plane is determined by the concentrations of the positive ions in the following way. Every point on the line AD, AE represents the composition of a salt mixture which contains the single positive ion $\overset{+}{A}$, every point on the line BD, BE that of a salt mixture which contains the single positive ion $\overset{+}{B}$, and every point on the line CD, CE that of a salt mixture which contains the single positive ion $\overset{+}{C}$. The points L, M and N represent, therefore, salt mixtures which have the following compositions as far as concerns their content of positive ions:

$$\begin{array}{rrrl} 100\overset{+}{A}, & 0\overset{+}{B}, & 0\overset{+}{C}, & (L) \\ 0\overset{+}{A}, & 100\overset{+}{B}, & 0\overset{+}{C}, & (M) \\ 0\overset{+}{A}, & 0\overset{+}{B}, & 100\overset{+}{C}, & (N) \end{array}$$

The point L represents a mixture of salts which contains, besides a definite mixture of negative ions, only the positive ion $\overset{+}{A}$; the point M represents a mixture of salts which contains, besides this same mixture of negative ions, only the positive ion $\overset{+}{B}$; and the point N represents a salt mixture which contains, besides this mixture of negative ions, only the positive ion $\overset{+}{C}$. It is clear that a point such as P, which lies in the section LMN, must represent a salt mixture that contains, besides the definite mixture of the two negative ions, a definite mixture of the three positive ions; namely, a mixture the composition of which is determined in the usual way by the position of the point P with respect to the sides of the equilateral triangle LMN. Of the total positive ions, the percentage x, of the ion $\overset{+}{A}$, which is contained by the salt mixture P is measured by the distance of the point P from the side MN, opposite to the vertex L, which represents the pure ion $\overset{+}{A}$ (associated, of course, with the definite mixture of negative ions). The percentage y, of the ion B, is measured by the distance of the point P from the side LN, opposite to the vertex M, which represents the pure ion $\overset{+}{B}$; the percentage $100 - \overline{x + y}$, of the third positive ion $\overset{+}{C}$, must then be measured by the distance of the point P from the side LM, opposite to the vertex N, which represents the pure ion $\overset{+}{C}$.

Summarising, we see that a mixture of the composition represented by the form 1 is partially represented by a point within the prism in the following way. The water content m is neglected. A section of the prism parallel to the triangular faces is chosen such that it divides the edges AD, AE; BD, BE; and CD, CE into two parts which represent the concentrations of the two negative ions in the negative ion mixture:

$$z\overset{-}{D}, 100 - z\overset{-}{E}.$$

The desired point lies in this section, and it is situated so as to represent the composition of the positive ion mixture:

$$x\overset{+}{A}, y\overset{+}{B}, 100 - \overline{x + y}\overset{+}{C},$$

by reference to the sides of the equilateral section, in the way which we have always used for representing the compositions of ternary mixtures.

The point AD, since it lies on the face AD, BD, CD, represents a "salt mixture" which contains the single negative ion $\overset{-}{D}$; and since it lies also on the line AD, AE it represents a "mixture" which contains the single positive ion $\overset{+}{A}$. The point AD represents, therefore, the pure salt AD, or, more strictly, the solution saturated with the pure salt AD at a

certain temperature. In the same way it will be seen that the remaining five corners of the prism represent the saturated solutions of the remaining five simple salts which can occur as solid phase in the quinary system. Points on an edge of the prism represent saturated solutions in a ternary system formed by water and two salts with a common ion; there are nine such ternary systems forming the basis of the quinary system, and these are represented, at the temperature of the isotherm, one on each of the nine edges of the prism. There are five quaternary systems which form the basis of the quinary system, and saturated solutions in these are represented on the faces of the prism. Of the five quaternary systems, two are formed by water and three salts with a common ion:

$$W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{-}\overset{-}{D}$$

and

$$W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{-}\overset{-}{E}.$$

They are represented one on each of the triangular faces of the prism. The remaining three quaternary systems are formed by water and reciprocal salt pairs,

$$W\text{-}(\overset{+}{A}, \overset{+}{B})\text{-}(\overset{+}{D}, \overset{+}{E})$$

$$W\text{-}(\overset{+}{A}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E}),$$

and

$$W\text{-}(\overset{+}{B}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E}).$$

They are represented one on each of the square faces of the prism.

§ 81. The isothermal conditions of equilibrium in the system

$$W\text{-}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E}),$$

when the only solid phases which can occur are the six simple salts, may be represented by Fig. 148. The isotherms in the five quaternary systems which form the basis of this quinary system are represented, by Jänecke's method, on the faces of the prism; the quinary saturation curves are marked in heavy line, in this figure, in order that they may be easily distinguished from the quaternary saturation curves. The isotherms in the two quaternary systems which are formed by water and three salts with a common ion are to be found in the two triangular faces of the prism; they may be compared with the simple quaternary type depicted in Fig. 82. The isotherms in the systems which are formed by water and two reciprocal pairs are to be found in the three square faces of the prism, and they may be compared with the quaternary type depicted in Fig. 112.

The quaternary system *W–AD–BD–CD* is represented at the temperature of the isotherm (Fig. 148), by the three saturation curves *PF*, *PG*, *PH*, and the invariant point *P*, which represents the solution saturated with the three salts *AD* + *BD* + *CD*. The quaternary system *W–AE–BE–CE* is represented by the three saturation curves *QJ*, *QK*, *QL*, and the invariant point *Q*. In the quaternary system formed by water and the reciprocal salt pairs *AD*, *BE* and *AE*, *BD*, which is depicted on the front square face of the prism, the two salts *AD* and *BE* are represented as constituting the stable pair; solutions saturated with this stable pair are represented by points on the quaternary saturation curve *RS*, whilst the quaternary invariant points *R* and *S* represent solutions saturated with the salt triads *AD* + *BE* + *BD* and *AD* + *BE* + *AE* respectively. The quaternary system formed by water and the reciprocal pairs *AE*, *CD* and *AD*, *CE* is depicted on the back face of the prism, and the two salts *AE* and *CD* are here represented as the stable pair; solutions saturated with this pair are represented by points on the quaternary saturation curve *TU*, whilst the quaternary invariant points *T* and *U* represent solutions saturated with the salt triads *AE* + *CD* + *AD* and *AE* + *CD* + *CE* respectively. Finally, the quaternary system formed by water and the reciprocal pairs *CD*, *BE* and *CE*, *BD* is depicted on the base of the prism, and the two salts *CD* and *BE* are represented as the stable pair; solutions saturated with this pair are represented by points on the quaternary saturation curve VW, whilst the quaternary invariant points *V* and *W* represent solutions saturated with the salt triads *CD* + *BE* + *BD* and *CD* + *BE* + *CE* respectively.

We see that there are eight quaternary invariant points in the quinary isotherm (Fig. 148), and each of these must form the starting point of a quinary saturation curve, the points of which represent solutions in equilibrium with three solid phases; the quinary saturation curves must end, within the prism, in quinary invariant points which represent solutions saturated with four solid phases. The nature of the fourth solid phase the appearance of which corresponds with the termination of a quinary saturation curve can be determined when the six simple salts alone appear as solid phases, and when the relations in the fundamental quaternary systems are known. We saw in § 70 that the four salts which constitute two reciprocal salt pairs (for example, *AD*, *BE*, *AE*, and *BD*) may all exist, at a quaternary transition point, in equilibrium with one another, and with a quaternary invariant solution. The equilibrium at such a transition point is represented by the following scheme:

$$AD + BE \rightleftarrows AE + BD.$$

It is an equilibrium which involves only the solid phases, an equilibrium in which the solution takes no part. In this respect, the transition point of the reciprocal pairs is strictly analogous to that of the anhydrous double salt in the ternary and quaternary systems (*cf.* § 60). It follows, namely, that the transition temperature of the reciprocal pairs is the same, in the quaternary, as in the quinary system. In addition to the four salts of the reciprocal pairs, a fifth solid phase will certainly be necessary for the definition of a quinary system invariant point (§ 77), but the temperature of the equilibrium cannot be affected by the presence of a quinary liquid phase and an additional solid phase which take no part in the equilibrium reactions. If the temperature of an isotherm is below the quaternary transition point of two reciprocal pairs, it is also below the quinary transition point of those pairs, and if, as a consequence, two salts are incompatible in the quaternary system, they must also be incompatible in the quinary system.

We will now return to the isotherm shown in Fig. 148. The point *P* represents the quaternary invariant solution saturated with the three salts $AD + BD + CD$, and the curve *PX*, which radiates from this point, is the quinary saturation curve of these three salts. It ends in the quinary invariant point *X*, where a fourth salt appears as a solid phase; this fourth solid phase, since we assume the absence of compounds, must be one of the three remaining simple salts AE, BE, or CE. Now it can be seen from the figure that the salt AE is incompatible with the salt BD in the quaternary system $W\text{-}(\overset{+}{A}, \overset{+}{B})\text{-}(\overset{-}{D}, \overset{-}{E})$, which is represented on the front face of the prism. The salt CE is incompatible with BD in the quaternary system

$$W\text{-}(\overset{+}{B}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E}),$$

which is represented on the base of the prism. Both AE and CE are, therefore, also incompatible with BD in the quinary system, and a quinary solution which is in equilibrium with the salt triad $AD+BD+CD$ cannot simultaneously be in equilibrium with either AE or CE. The only salt which can appear as a fourth solid phase in equilibrium with these three is BE. It can, in fact, be seen that this salt is compatible with AD in the system $W\text{-}(\overset{+}{A}, \overset{+}{B})\text{-}(\overset{-}{D}, \overset{-}{E})$, with CD in the system $W\text{-}(\overset{+}{B}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E})$, and of necessity with BD, since the two, having an ion in common, cannot react.

The point X represents, then, the quinary invariant solution which is saturated with the four salts:

$$AD + BD + CD + BE.$$

From it, there must diverge the saturation curves of those salt triads which can be obtained from the four salts by taking three at a time. There are four such salt triads, namely:

$AD + BD + CD$ . . . . 1.
$AD + BD + BE$ . . . . 2.
$BD + CD + BE$ . . . . 3.
and $AD + CD + BE$ . . . . 4.

The curve XP is, as we have already seen, the saturation curve of the three salts $AD + BD + CD$ (1), and it ends on a face of the prism, at the invariant point P in the quaternary system $W\text{-}AD\text{-}BD\text{-}CD$. The curve XS ends on the front face of the prism, in the quaternary invariant point S, which represents a solution in equilibrium with the three salts $AD + BD + BE$; it is, therefore, the saturation curve of this salt triad (2).

Similarly, the curve XV is the saturation curve of the salt triad $BD + CD + BE$ (3), since it ends in the invariant point V, which represents a quaternary solution in equilibrium with these salts. There is no point, *on the faces of the prism*, which represents a quaternary solution in equilibrium with the three salts $AD + CD + BE$ (4); this salt triad, unlike those which may appear at the invariant points in the fundamental quaternary systems, contains all five ions, and its saturation curve must end *within* the prism, in a second quinary invariant point. At this invariant point one of the three remaining simple salts BD, AE, or CE must appear as a fourth solid phase; of these, we may exclude the salt BD, since it occurs in equilibrium with the salt triad 4, at the first invariant point X; the salt CE must also be excluded, since it is incompatible with the salt AD in the quaternary system $W\text{-}(\overset{+}{A}, \overset{+}{C})\text{-}(\overset{-}{D}, \overset{-}{E})$. The saturation curve XY, of the salt triad 4, ends, therefore, in a second invariant point Y, where the salt AE appears as a fourth solid phase. The salts in equilibrium with a quinary solution at the invariant point Y are:

$$AD + CD + BE + AE$$

(Salt triad 4 + AE)

The following salt triads can be formed from these four salts by taking three at a time, and the corresponding saturation curves must diverge from the invariant point Y:

$AD + CD + BE$ . . . . 4.
$AD + CD + AE$ . . . . 5.
$AD + BE + AE$ . . . . 6.
$CD + BE + AE$ . . . . 7.

We have already considered the saturation curve YX of the salt triad $AD + CD + BE$ (4), and we have seen that it is bounded *at each end* by a quinary invariant point. The curve YT is the saturation curve of the salt triad

$$AD + CD + AE \text{ (5)},$$

since it ends on the back face of the prism, in the invariant point T, which represents the quaternary solution in equilibrium with this salt triad. Similarly, the curve YR is the saturation curve of the salt triad $AD + BE + AE$ (6), since it ends on the front face of the prism, in the invariant point R, which represents the quaternary solution in equilibrium with these salts. There exists no point *on the faces of the prism* which represents a quaternary solution in equilibrium with the salt triad $CD + BE + AE$ (7); these salts also contain all five ions, and the corresponding saturation curve must also end, at each extremity, in a quinary invariant point. At this third invariant point one of the three salts AD, CE, or BD (no one of which is contained by the salt triad 7) must occur as a fourth solid phase. Proceeding as before, we find that we must exclude the salt AD because it forms the fourth solid phase at the invariant point Y, and the salt BD because it is incompatible with AE in the quaternary system

$$W\text{-}(\overset{+}{A}, \overset{+}{B})\text{-}(\overset{-}{D}, \overset{-}{E}).$$

The third quinary invariant point Z represents, therefore, a solution in equilibrium with the following four salts:

$$CD + BE + AE + CE$$

(Salt triad 7 + CE).

The curve YZ is the saturation curve of the salt triad 7, and it is bounded by the two quinary invariant points Y and Z. The saturation curves of the following salt triads must diverge from the point Z:

$CD + BE + AE$ . . . . . 7.
$CD + BE + CE$ . . . . . 8.
$CD + AE + CE$ . . . . . 9.
$BE + AE + CE$ . . . . . 10.

The curve ZW is the saturation curve of the salt triad $CD + BE + CE$ (8), since it ends on the base of the prism, in the point W, which represents the quaternary invariant solution in equilibrium with these salts. This curve ZU is the saturation curve of the salt triad $CD + AE + CE$ (9), since it ends on the back face of the prism, in the quaternary invariant point U, and the curve ZQ is the saturation curve of the salt triad $BE + AE + CE$ (10), since it ends on the triangular face of the prism, in the quaternary invariant point Q.

We have shown that there are ten quinary saturation curves in this simple type of quinary isotherm; points on these curves represent solutions which are in equilibrium with three solid phases. The saturation curves bound saturation surfaces the points of which represent solutions which are in equilibrium with two solid phases, and the saturation surfaces bound spaces the points of which represent solutions which are in equilibrium with one solid phase. The quinary saturation surfaces and spaces can be distinguished more clearly in Fig. 149, where the quinary isotherm is dissected into the various spaces. It can be seen that, to the six corners of the prism, which represent the binary solutions saturated with each of the six simple salts at the temperature of the isotherm, there correspond six saturation spaces; the points in these spaces represent the quinary solutions saturated with each of the six simple salts at the temperature of the isotherm.

We will suppose that, in the isotherm of Fig. 148, a plane is laid through the corners *AD*, *CD*, and *BE*, as shown in that figure. It will be found, on examination, that this plane intersects only the quinary saturation spaces of *AD*, *CD*, and *BE*. These three are, therefore, the only salts which can occur as solid phases in the system *W–AD–CD–BE*, and this system is a true quaternary system; it will be possible to express the composition of all phases which result on mixing water and the three salts *AD*, *CD*, and *BE* in terms of these four substances. It is to be observed, nevertheless, that the three salts *AD*, *CD*, and *BE* contain all the five ions of the quinary system; of the six salts which can be formed from the five ions, the only ones which can occur as solid phases in the system *W–AD–CD–BE* are the three salts *AD*, *CD*, *BE* themselves. The isotherm in this quaternary system is given by the intersection of the plane *AD,CD,BE* with the quinary saturation spaces, surfaces and curves. It is represented, in the figure, by the *quaternary* invariant point *e*, in which the plane *AD,CD,BE* intersects the quinary saturation curve *XY* of $AD + CD + BE$, and by the *quaternary* saturation curves *eb*, *eg*, and *eG*, in which the plane intersects the quinary saturation surfaces of $AD + BE$, $CD + BE$, and $AD + CD$ respectively.

It will be found, in the same way, that a plane which is laid through the corners *AE*, *CD*, *BE* of the prism intersects only the saturation spaces of these three salts. The system *W–AE–CD–BE* is, therefore, also a true quaternary system, despite the fact that the three salts again contain all the five ions of the quinary system. The point *f* in Fig. 148 is the quaternary invariant point, and the curves *fh*, *fg*, *fJ* the quaternary saturation curves, in this system.

We see that these two plane sections of the quinary isotherm (*AD,CD,BE* and *AE,CD,BE*) represent the conditions of equilibrium in two systems of a lower order, namely, in two quaternary systems. The quinary isotherm is divided by the two planes, into three parts, which give the isothermal relations in three quinary systems of the simplest type, namely that discussed in § 79 and illustrated in Fig. 143. This can be seen clearly from Fig. 150, where the prism of Fig. 148 is dissected into three tetrahedra. The isotherm in the quinary system *W–AD–BD–CD–BE* is represented in Fig. 150, within the tetrahedron *AD*, *BD*, *CD*, *BE*; it is strictly comparable with the isotherm of Fig. 143, and contains only one quinary invariant point; the face *AD,CD,BE* of this tetrahedron contains the isotherm in the quaternary system *W–AD–CD–BE*, an isotherm which, as we have seen, is obtained as a plane section of the quinary isotherm in Fig. 148. Similarly, the quinary systems *W–AD–AE–CD–BE* and *W–AE–CD–BE–CE* are represented within the corresponding tetrahedra of Fig. 150, and they also show the simplest isothermal type.

We saw (§ 74) that the isotherm in a quaternary system of the type $W\text{–}(\overset{+}{A},\overset{+}{B})\text{–}(\overset{-}{D},\overset{-}{E})$, can sometimes be divided by a linear section, into the isotherms in two simpler quaternary systems; this is only possible when the two quaternary invariant points represent congruently saturated solutions. In the same way, the isotherm in the quinary system $W\text{–}(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})\text{–}(\overset{-}{D}, \overset{-}{E})$ can be divided, by plane sections, into the isotherms in three simpler quinary systems, only when the three quinary invariant points represent congruently saturated solutions. The point *X* (Fig. 150) represents, for example, the invariant solution which is saturated with the four salts $AD + BD + CD + BE$; and since the point lies within the tetrahedron *AD*, *BD*, *CD*, *BE*, the solution is congruently saturated. If the point *X* lay outside the tetrahedron *AD*, *BD*, *CD*, *BE*, the solution *X*

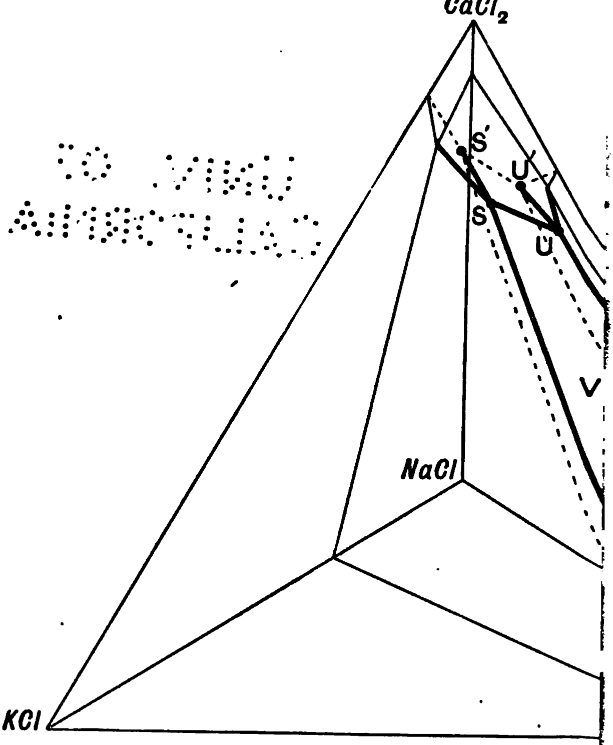


Fig. 152.

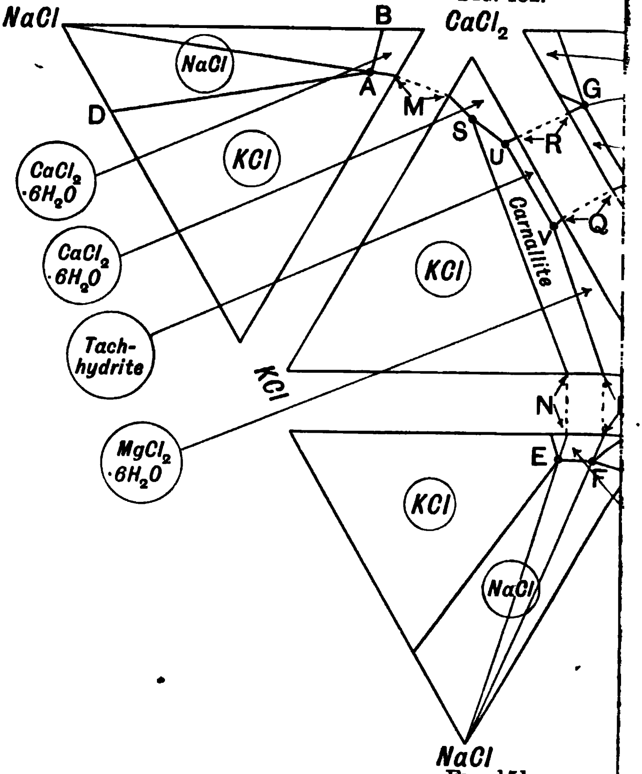


Fig. 151.

SHEET XXI.

would be incongruently saturated, and it would then be impossible to divide the isotherm of Fig. 148 into three simpler isotherms, as we have done in Fig. 150.

Each of the saturation spaces contained within the three tetrahedra of Fig. 150 can be projected upon a face of the containing tetrahedron, as described in § 79 for the simplest quinary isothermal type; the nine projections obtained in this way (three for each tetrahedron) will give a plane representation of the quinary isotherm of Fig. 148.

§ 82. The only published investigations of the conditions of heterogeneous equilibria in systems of five independent components are to be found in van't Hoff's works on the oceanic salt deposits.[1] The chief salt constituents of sea water are the four metals sodium, magnesium, potassium, and calcium in the form of their chlorides and sulphates. The average composition of sea water, expressed in equivalents, and by Jänecke's method, is approximately the following

$$(180{,}600H_2O), (77{\cdot}0Na_2, 17{\cdot}9Mg, 3{\cdot}5Ca, 1{\cdot}6K_2), (90{\cdot}8Cl_2, 9{\cdot}2SO_4).$$

The system formed by water, these four positive, and two negative ions is clearly one of six independent components. We shall briefly consider two of the quinary systems which are of fundamental importance for the study of this six component system. The solutions of the oceanic salts form an exceedingly complicated system owing to the large number of binary and ternary compounds which can occur as solid phases; the investigation of this system, in so far as it is necessary for the study of the oceanic salt deposits, is simplified, however, by the following considerations. It can be seen that, of the total positive ions present in sea water, 77 per cent. is formed by sodium, and, of the total negative ions, 90·8 per cent. is formed by chlorine. The first salt to separate when sea water is concentrated is, therefore, sodium chloride, and it is clear that any salt which has been deposited by the evaporation of water from the ocean must have been deposited in the presence of sodium chloride as a solid phase; for the purpose of this study it is, in other words, only necessary to consider the saturation space of sodium chloride in a quinary isotherm, the saturation surfaces which bound this space, and the curves and points in which these surfaces meet. The problem is still further simplified by the fortunate fact that sodium chloride forms no binary or ternary compound with any of the other salts; the projection of the saturation space of sodium chloride in a quinary isotherm will have, therefore, the same form as the quaternary isotherm in the system formed by water and the salts *without* sodium chloride (*cf.* § 79).

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[1] An account of these investigations is given by van't Hoff in his book "Zur Bildung der Ozeanischen Salzablagerungen."

The isotherm in the quinary system

$$H_2O\text{–}NaCl\text{–}MgCl_2\text{–}KCl\text{–}CaCl_2$$

may be represented within a tetrahedron the corners of which represent the binary saturated solutions of the four salts $NaCl$, $MgCl_2$, KCl and $CaCl_2$; these salts all contain, namely, the common chlorine ion, and the system is of the type discussed in § 79. In order to secure a clear picture, the four triangular faces of this tetrahedron are shown, in Fig. 151, in the same plane, and slightly separated from each other. The tetrahedron could be constructed from this plane figure if the three outside triangles were cut out from the paper, along the sides which meet in the three $NaCl$ vertices; it would then only be necessary to bend these three triangles out of the plane of the paper, by folding them along the three sides which they have in common with the inner triangle, in order to make the three $NaCl$ vertices coincide in one point—the vertex of the regular tetrahedron whose base is the inner triangle $CaCl_2$, KCl, $MgCl_2$.

The conditions of equilibrium which are represented diagrammatically in Fig. 151 are those which obtain at 25°. We will consider first the quaternary isotherms which are to be found on the faces of the tetrahedron. The quaternary system $H_2O\text{–}NaCl\text{–}KCl\text{–}CaCl_2$ is represented at 25° in the triangle $NaCl$, KCl, $CaCl_2$ of Fig. 151. It is of the simplest type, and can be compared with Fig. 82 of the previous chapter; the only solid phases which occur in this system are the two simple salts $NaCl$, KCl, and the simple salt hydrate $CaCl_2.6H_2O$.

The isotherm in the quaternary system $H_2O\text{–}NaCl\text{–}MgCl_2\text{–}KCl$ is represented within the triangle $NaCl$, $MgCl_2$, KCl, and it shows the saturation surface of the hydrated double salt carnallite ($KCl.MgCl_2.6H_2O$), in addition to those of the simple salts NaCl, KCl, and the simple salt hydrate $MgCl_2.6H_2O$; this isotherm has already been discussed in § 76, and represented in Fig. 135.

The isotherm in the quaternary system H_2O–NaCl–$MgCl_2$–$CaCl_2$ is represented within the triangle NaCl, $MgCl_2$, $CaCl_2$. It also shows the saturation surface of a ternary compound—tachhydrite, $CaCl_2.2MgCl_2.12H_2O$, which occurs as a solid phase in the ternary system H_2O–$CaCl_2$–$MgCl_2$; the double salt tachhydrite is strictly comparable with carnallite, the compound which occurs in the ternary system H_2O–KCl–$MgCl_2$, as will be seen more readily if the formula of carnallite is written $2KCl.2MgCl_2.12H_2O$. In the quaternary system H_2O–NaCl–$MgCl_2$–$CaCl_2$ at 25°, there occurs also a very small saturation surface of the tetrahydrate of calcium chloride $CaCl_2.4H_2O$, but, for simplicity, this is not represented in Fig. 151.

The three quaternary isotherms which we have briefly described all contain a sodium chloride saturation surface. In the quinary isotherm, these surfaces must form the boundaries, in the faces of the tetrahedron, of the quinary saturation space of sodium chloride. We have already explained that this space with its bounding surfaces and curves is the only part of the quinary isotherm which is of importance for the study of the oceanic salt deposits. Its projection upon the base of the tetrahedron is shown in the inner triangle $CaCl_2$, KCl, $MgCl_2$ of Fig. 151. The sides of this triangle represent the projections of the saturation curves which bound the quaternary saturation surfaces of sodium chloride. Thus, in the quaternary system H_2O–NaCl–KCl–$CaCl_2$(represented in the triangle $NaCl_2$, KCl, $CaCl_2$) the saturation surface of NaCl is bounded by the saturation curve *AD* of NaCl + KCl, and the saturation curve *AB* of NaCl + $CaCl_2.6H_2O$. The projections of these curves upon the base are given by the two sections of the base line KCl,*M* and *M*,$CaCl_2$, whilst the point *M* is the projection, through the NaCl vertex, of the quaternary invariant point *A*, which represents the quaternary solution in equilibrium with NaCl + KCl + $CaCl_2.6H_2O$. The line KCl,*M* in the inner triangle (the projection of the quinary saturation space of sodium chloride) bounds, therefore, the quinary saturation surface of NaCl + KCl; the line *M*,$CaCl_2$ bounds that of NaCl + $CaCl_2.6H_2O$; and the point *M* forms the starting point of the quinary saturation curve of NaCl + KCl + $CaCl_2.6H_2O$.

Since we are representing in the inner triangle only the saturation surfaces and curves which bound the [quinary saturation space of sodium chloride, it is to be understood that every point in it represents a solution in equilibrium with this solid phase, and we have marked only the additional solid phases with which solutions are saturated. Thus, the surface KCl,*MSN*, which is bounded by the projection KCl,*M* of the quaternary saturation curve *AD*, is the quinary saturation surface of NaCl + KCl although it is only marked with the solid phase KCl in the figure. Similarly, points on the surface $CaCl_2$,*MSUR* represent solutions saturated with $CaCl_2.6H_2O$ in the presence of solid sodium chloride, and points on the curve *MS* solutions saturated with KCl + $CaCl_2.6H_2O$, also in the presence of sodium chloride as a third solid phase.

The saturation curves which bound the saturation surfaces of sodium chloride in the two remaining quaternary isotherms are projected in the same way upon the side of the triangle opposite to the NaCl vertex. Thus the sections KCl,*N*; *NP*; *P*,$MgCl_2$, of the side KCl,$MgCl_2$, are the projections of the saturation curves of KCl + NaCl, Carnallite + NaCl, and $MgCl_2.6H_2O$ + NaCl, respectively, in the quaternary system H_2O–NaCl–KCl–$MgCl_2$. They bound the quinary saturation surfaces KCl,*MSN*, of KCl + NaCl, *NSUVP*, of Carnallite + NaCl, and *PVQ*,$MgCl_2$, of $MgCl_2.6H_2O$ + NaCl. The sections $MgCl_2$,*Q*; *QR*; and *R*,$CaCl_2$, of the side $MgCl_2$,$CaCl_2$, are the projections of the saturation curves of $MgCl_2.6H_2O$ + NaCl, Tachhydrite + NaCl, and $CaCl_2.6H_2O$ + NaCl, in the quaternary system H_2O–NaCl–$MgCl_2$–$CaCl_2$. They bound the quinary saturation surfaces the points of which represent quinary solutions saturated with $MgCl_2.6H_2O$, tachhydrite, and $CaCl_2.6H_2O$ respectively, in addition to sodium chloride as a second solid phase.

There are seven quinary saturation curves which bound the quinary saturation space of sodium chloride, and these are represented by *MS*, *NS*, *PV*, *QV*, *RU*, *SU*, and *UV*. They intersect, by groups of three, in the three quinary invariant points S, U, and V, which represent solutions in equilibrium with four solid phases. The point S represents a solution saturated with

$$KCl + CaCl_2.6H_2O + \text{Carnallite} + NaCl;$$

the point U a solution saturated with

$$CaCl_2.6H_2O + \text{Carnallite} + \text{Tachhydrite} + NaCl;$$

and the point V a solution saturated with

$$MgCl_2.6H_2O + \text{Carnallite} + \text{Tachhydrite} + NaCl.$$

We have represented in the inner triangle of Fig. 151 the projection of the quinary saturation space of sodium chloride. In the tetrahedron which represents the complete quinary isotherm (and not only the saturation space of sodium chloride), this triangle must contain the isotherm in the quaternary system H_2O–$CaCl_2$–KCl–$MgCl_2$. We have not considered this system in our previous discussion, for, since it contains no sodium chloride, it cannot yield solutions which are saturated with this salt; the quinary saturation space of sodium chloride cannot, in other words, extend into the base of the tetrahedron. It follows, however, from the conclusions of § 79, that, since sodium chloride forms no compounds with either of the remaining three salts KCl, $CaCl_2$, or $MgCl_2$, the projection of the quinary saturation space of sodium chloride is identical in form with the quinary isotherm in the system H_2O–KCl–$CaCl_2$–$MgCl_2$. Since Fig. 151 is only diagrammatic, the inner triangle can, therefore, represent equally well either the boundary of the quinary saturation space of sodium chloride or the isotherm in the quaternary system H_2O–KCl–$CaCl_2$–$MgCl_2$. Thus, the point S may be taken to represent either a *quinary* invariant solution saturated with the *four* salts

$$KCl + CaCl_2.6H_2O + \text{Carnallite} + NaCl,$$

or a *quaternary* invariant solution saturated with the *three* salts

$$KCl + CaCl_2.6H_2O + \text{Carnallite},$$

sodium chloride being absent. In a picture which represented the true quantitative relations (not merely a diagrammatic figure), the actual positions of the points S, U, and V would depend upon whether these points represented quaternary or quinary invariant solutions; the form of the picture would, however, remain the same.

The following considerations will, perhaps, make this clearer. It is seen that three saturation curves intersect in each of the invariant points *S*, *U*, and *V* of Fig. 151. If these points represent quinary invariant solutions, a fourth saturation curve must radiate from each. Since this curve is not one of those which bound the saturation space of sodium chloride, it is not represented in Fig. 151. For example, from the quinary invariant point *S* a fourth saturation curve must diverge, namely, a curve the points of which represent quinary solutions saturated with the three salts

$$KCl + CaCl_2.6H_2O + \text{Carnallite},$$

which do not include sodium chloride. This curve must end in a corresponding quaternary invariant point *S'* on the base of the tetrahedron, but since we have projected the saturation space of sodium chloride upon this base, we cannot represent the point *S'* in Fig. 151 without sacrificing the clarity of the figure. Similarly, there corresponds with the quinary invariant point *U* a quaternary invariant point *U'* on the base of the tetrahedron, which represents a quaternary solution saturated with

$$CaCl_2.6H_2O + \text{Carnallite} + \text{Tachhydrite},$$

and a quinary saturation curve *UU'*, the points of which represent quinary solutions saturated with these three salts; to the quinary invariant point *V* there corresponds a quaternary invariant point *V'* which represents a quaternary solution saturated with

$$MgCl_2.6H_2O + \text{Carnallite} + \text{Tachhydrite},$$

and a quinary saturation curve *VV'*, the points of which represent quinary solutions saturated with these three salts.

The complete quinary isotherm is represented within the tetrahedron $NaCl, CaCl_2, KCl, MgCl_2$ in Fig. 152; the tetrahedron is viewed from above, and the NaCl vertex is to be considered as lying above the plane of the paper, which contains the base $CaCl_2$,KCl,$MgCl_2$ of the tetrahedron. The quinnary saturation curves are drawn in heavy line, and the dotted lines are the quaternary saturation curves in the system H_2O–KCl–$CaCl_2$–$MgCl_2$, which is represented on the base. The points S′, U′, V′ in this quaternary isotherm are the quaternary invariant points discussed above, and the lines *SS′*, *UU′*, *VV′* are the quinary saturation curves which do not bound the saturation space of sodium chloride.

We will now consider the conditions of equilibrium in the quinary system H_2O–(Na_2,K_2,Mg)–(Cl_2,SO_4), which belongs to the type discussed in § 81. The six simple salts which can occur as solid phases in the system are: NaCl, KCl, $MgCl_2$, Na_2SO_4, K_2SO_4, and $MgSO_4$, and the binary saturated solutions

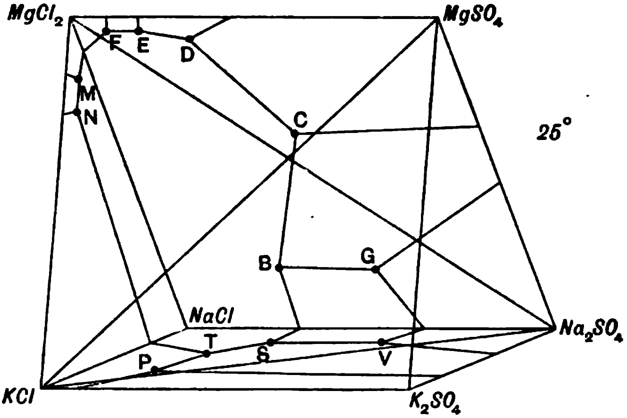

Fig. 153.

of these salts at 25° are represented by the corners of a prism in Fig. 153; the three chlorides are represented on one triangular face of the prism, the three sulphates on the other, in accordance with the method of representation described in § 81. In that paragraph, we showed that the prism could be divided by two triangular sections into three tetrahedra; for example, in the case here considered, by the planes $MgCl_2$,KCl,Na_2SO_4, and $MgSO_4$,KCl,Na_2SO_4, into the tetrahedra NaCl, $MgCl_2$, KCl, Na_2SO_4; $MgCl_2$, KCl, Na_2SO_4, $MgSO_4$; and $MgSO_4$,KCl,Na_2SO_4,K_2SO_4. Further, we have then pointed out in § 81 that, in the simplest case, the systems formed by water and the groups of four salts represented by the corners of such tetrahedra constitute quinary systems of the simplest type; namely, quinary systems which can be represented within the corresponding tetrahedra, and the behaviour of which is, therefore, similar to that of systems formed by water and four salts with a common ion. If, in the present example, the system H_2O–NaCl–$MgCl_2$–KCl–Na_2SO_4 were a quinary system of this simple type, the saturation space of sodium chloride would be completely confined to the tetrahedron NaCl, $MgCl_2$, KCl, Na_2SO_4, and the four faces of this tetrahedron would represent quaternary systems of simple type; in particular, the system H_2O–$MgCl_2$–KCl–Na_2SO_4 would behave as a true quaternary system, and the corresponding isotherm would be given by the triangular section of the quinary isotherm through the corners $MgCl_2$, KCl, and Na_2SO_4 of the prism; finally, this quaternary isotherm would be identical in form with the projection of the quinary saturation space of sodium chloride upon the face $MgCl_2$,KCl,Na_2SO_4, of the tetrahedron NaCl, $MgCl_2$, KCl, Na_2SO_4. If these relations held, the investigation of the quinary saturation space of sodium chloride would be no more difficult in the system H_2O–(Na_2,K_2,Mg)–(Cl_2,SO_4) than in the system H_2O–(Na_2,K_2,Mg,Ca)–Cl_2, where all salts possessed the same negative ion; it would only be necessary to investigate the system H_2O–$MgCl_2$–KCl–Na_2SO_4 (supposed quaternary), and then to redetermine the various saturation curves and points in this system, in the presence of such an excess of the fifth component, sodium chloride, as to insure its existence as a solid phase in equilibrium with all solutions.

The relations are, however, not of this simple nature, as we shall see from a consideration of Fig. 153. On corresponding faces of the prism in this figure there are shown the isotherms in the three quaternary systems H_2O–(Na_2,K_2,Mg)–Cl_2,H_2O–(Na_2,Mg)–(Cl_2,SO_4), and H_2O–(Na_2,K_2)–(Cl_2,SO_4). These quaternary isotherms have been discussed in the previous chapter, and they have already been represented in Figs. 135, 142, and 139, to which the reader should refer. The isotherm in the quaternary system H_2O–(Na_2,Mg)–(Cl_2,SO_4) is represented on the back face of the prism, and it is divided by the diagonal $MgCl_2$, Na_2SO_4 into two parts NaCl,$MgCl_2$,Na_2SO_4 and $MgSO_4$,$MgCl_2$, Na_2SO_4, of which the first forms a face of the tetrahedron NaCl, $MgCl_2$, KCl, Na_2SO_4.

XXII.

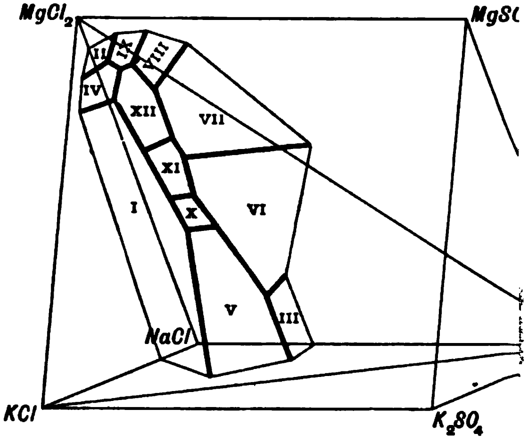

FIG. 155.

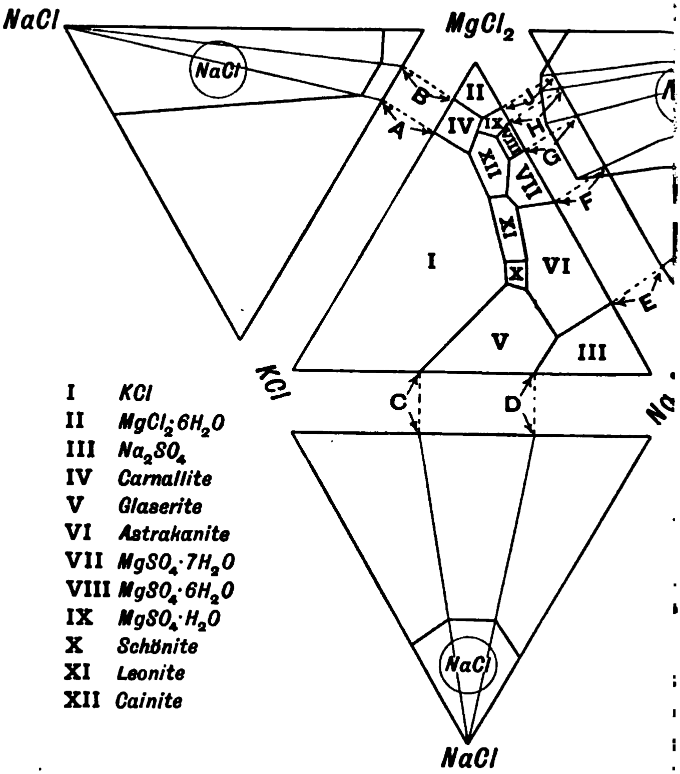

FIG. 154.

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The two parts into which this quaternary isotherm is divided by the diagonal do not represent, however, the isotherms in two simpler quaternary systems; the two systems

H_2O–$NaCl$–$MgCl_2$–Na_2SO_4 and H_2O–$MgSO_4$–$MgCl_2$–Na_2SO_4

cannot, namely, be considered as quaternary systems of a simple type, since, for example, the quaternary saturation surface of sodium chloride is not confined to the triangle, $NaCl$, $MgCl_2$, Na_2SO_4, but extends into the triangle $MgSO_4$, $MgCl_2$, Na_2SO_4; this results from the fact that the invariant solutions are incongruently saturated, as we saw when discussing quaternary systems of this type. Now since the quaternary saturation space of sodium chloride extends outside the triangle $NaCl$, $MgCl_2$, Na_2SO_4, which forms one of the faces of the tetrahedron $NaCl$, $MgCl_2$, KCl, Na_2SO_4, it follows that the quinary saturation space of sodium chloride, which is bounded by this surface, must also extend outside the tetrahedron. The plane $MgCl_2$, KCl, Na_2SO_4 must, in fact, intersect the saturation space of sodium chloride, and this salt can, therefore, occur as a solid phase in the system H_2O–$MgCl_2$–KCl–Na_2SO_4; this system is, in other words, not a quaternary system, for it is not possible to express the composition of sodium chloride in terms of the three salts, $MgCl_2$, KCl, and Na_2SO_4 alone.

We see that the system H_2O–$NaCl$–$MgCl_2$–KCl–Na_2SO_4 is not a quinary system of a type which, like systems formed by salts with a common ion, can be represented *within* a corresponding tetrahedron; the saturation space of sodium chloride intersects the face $MgCl_2$,KCl,Na_2SO_4 of the tetrahedron $NaCl$, $MgCl_2$, KCl, Na_2SO_4, and the system H_2O–$MgCl_2$–KCl–Na_2SO_4 is not, therefore, a quaternary system. We may, however, still obtain a representation of the saturation space of sodium chloride in one plane, by projecting it upon the face $MgCl_2$,KCl,Na_2SO_4, opposite to the sodium chloride vertex, but the resulting figure will no longer resemble, in form, a quaternary isotherm; further, since the saturation space of sodium chloride extends on both sides of the plane $MgCl_2$,KCl,Na_2SO_4, it will be necessary to project some parts of the space from the side nearer the sodium chloride vertex on to this plane, and some parts from the side farther from the sodium chloride vertex.

Fig. 154 shows the four faces of the tetrahedron

$NaCl, MgCl_2, KCl, Na_2SO_4$ bent into one plane, in the way which we described for the tetrahedron $NaCl, KCl, MgCl_2, CaCl_2$ earlier in this paragraph. The inner triangle of this figure is the section $MgCl_2, KCl, Na_2SO_4$ of the prism in Fig. 153; the triangle $NaCl, KCl, MgCl_2$ represents the side face of this prism; the two remaining triangles represent parts of those two square faces of the prism which meet in the sodium chloride corner, namely, those parts which form the two remaining faces of the tetrahedron $NaCl, MgCl_2, KCl, Na_2SO_4$. This tetrahedron is, as a matter of fact, not regular, and the triangles which form its faces are not all equilateral. We have, however, so represented them in Fig. 154 for the sake of symmetry. In the three outer triangles of this figure, there are shown only those saturation curves which bound the saturation surfaces of sodium chloride in the three quaternary systems $H_2O–(Na_2,K_2,Mg)–Cl_2$, $H_2O–(Na_2,Mg)–(SO_4,Cl_2)$, and $H_2O–(Na_2,K_2)–(SO_4,Cl_2)$ (*cf.* Figs. 135, 142, and 139). We have already seen that the saturation surface of sodium chloride in the quaternary system $H_2O–(Na_2,Mg)–(SO_4,Cl_2)$ is not confined to the triangle $NaCl, MgCl_2, Na_2SO_4$ but extends outside it, as shown in Fig. 154.

The projection of the surfaces and curves which bound the quinary saturation space of sodium chloride are represented within the inner triangle $MgCl_2, KCl, Na_2SO_4$. We will consider first the sides of this triangle. They contain the projections, through the sodium chloride vertex, of the saturation curves which are contained in the outer triangles, and which bound the quaternary saturation surfaces of sodium chloride. Thus the part *AB* of the side $MgCl_2,KCl$ is the projection of the quaternary saturation curve of Carnallite + NaCl in the system $H_2O–(Na_2,K_2,Mg)–Cl_2$; the part *CD* of the side KCl,Na_2SO_4 is the projection of the quaternary saturation curve of Glaserite + NaCl in the system $H_2O–(Na_2,K_2)–(SO_4,Cl_2)$; the parts *EF*, *FG*, *GH*, *HJ* of the side $Na_2SO_4, MgCl_2$ are the projections of the quaternary saturation curves of Astrakanite + NaCl, $MgSO_4.7H_2O$ + NaCl, $MgSO_4.6H_2O$ + NaCl and $MgSO_4.H_2O$ + NaCl, respectively, in the system $H_2O–(Na_2,Mg)–(SO_4,Cl_2)$.

To each of these quaternary saturation curves there corresponds, within the inner triangle, a quinary saturation surface. For example, the quaternary saturation curve *AB*, of Carnallite + NaCl bounds the quinary saturation surface (IV) of Carnallite + NaCl, as shown in the figure; the quaternary saturation curve *CD* of Glaserite + NaCl bounds the quinary saturation surface (V) of this salt pair, and so with the remaining quaternary saturation curves. There can be seen, however, in the inner triangle of Fig. 154, the saturation surfaces (X, XI, XII) of three salts which cannot occur in either of the three fundamental quaternary systems. These salts are: Schönite, ($MgSO_4.K_2SO_4.6H_2O$), Leonite ($MgSO_4.K_2SO_4.4H_2O$) and Cainite ($MgSO_4.KCl.3H_2O$); and the quinary saturation surfaces of Schönite+NaCl, Leonite+NaCl, and Cainite+NaCl lie wholly within the triangle $MgCl_2$, KCl, Na_2SO_4. The saturation space of sodium chloride, if represented within the prism of Fig. 153, would, therefore, be bounded in parts by saturation surfaces which do not intersect any face of the tetrahedron NaCl, $MgCl_2$, KCl, Na_2SO_4. The three double salts schönite, leonite, and cainite occur as solid phases in the quaternary system H_2O–(K_2,Mg)–(SO_4,Cl_2), which we have discussed in the previous chapter and depicted in Fig. 141. This system would be represented on the front face of the prism in Fig. 153—a face which lies completely outside the tetrahedron NaCl, $MgCl_2$, KCl, Na_2SO_4. The quinary saturation spaces of schönite, leonite, and cainite must, therefore, be bounded by quaternary saturation surfaces in this front face, but *within the prism* they must meet the saturation space of sodium chloride in the three quinary saturation surfaces of Fig. 154. We see, again, that the behaviour of the system H_2O–NaCl–$MgCl_2$–KCl–Na_2SO_4 is not that of the simple quinary system formed by water and four salts with a common ion. The composition of none of these three double salts can be expressed in positive terms of NaCl, $MgCl_2$, KCl, and Na_2SO_4; in each case a negative value must be assigned to the concentration of sodium chloride; thus, for cainite ($MgSO_4.KCl.3H_2O$) we must write:

$$(MgCl_2 + KCl + Na_2SO_4 - 2NaCl).3H_2O,$$

and for schönite ($MgSO_4.K_2SO_4.6H_2O$), and leonite ($MgSO_4.K_2SO_4.4H_2O$):

$$(MgCl_2 + 2KCl + 2Na_2SO_4 - 4NaCl)aq.$$

The saturation space of sodium chloride with its bounding surfaces and curves is represented in Fig. 155 as a space figure within the prism. This figure should be compared with the inner triangle of Fig. 154, which is the projection of Fig. 155 upon the plane $MgCl_2$, KCl, Na_2SO_4.

It is clear that a graphical representation of the quinary isotherm is of little value for exhibiting the actual quantitative relations in the system. A plane representation, such as the projection of Fig. 154, can, for example, only be obtained by neglecting the concentrations both of water and of sodium chloride in the various saturated solutions. A picture which, whilst abandoning all attempts to represent quantitative relations, shows the true relative positions of the various saturation surfaces is of almost equal value for practical purposes. Such a picture is given in Fig. 156, which has been obtained from the projection of the saturation space of sodium chloride (Fig. 154) in the following way. The triangle $MgCl_2$, KCl, Na_2SO_4 of Fig. 154 has been replaced by a square in Fig. 156, the $MgCl_2$ vertex of the triangle being expanded into the upper side of the square. The various quinary saturation surfaces of Fig. 154 have been replaced in Fig. 156 by rectangular areas which possess no quantitative significance, but which

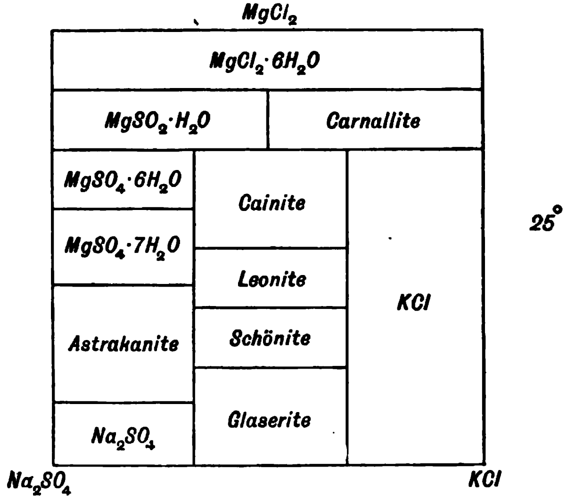

FIG. 156.

occupy the same positions in relation to one another as do the saturation surfaces in the projection. This can readily be seen from a comparison of the two figures; it will be found, for example, that the saturation surface of cainite in both figures is bounded by those of KCl, carnallite, $MgSO_4.H_2O$, $MgSO_4.6H_2O$, $MgSO_4.7H_2O$, and leonite, in order. The utility of Fig. 156 lies in the fact that it shows all the possible salts and combinations of salts which may exist at 25° in equilibrium with solid sodium chloride and saturated solutions. It shows, for example, that the combination astrakanite–cainite is not possible at 25°, since the saturation surfaces of these two salts are completely separated from each other by those of leonite and $MgSO_4.7H_2O$; the salts are, in other words, incompatible, and it has been proved experimentally that when they are brought into contact with each other in the presence of a suitable liquid phase they react to form the compatible pair Leonite + $MgSO_4.7H_2O$.

Diagrams similar to that given in Fig. 156 were used by van't Hoff for the qualitative representation of his results, and they were called by him "*Paragenese.*" Van't Hoff was able to construct a series of these diagrams which showed the salts and the salt combinations that could exist in equilibrium with solid sodium chloride and saturated solutions, at all temperatures between 0° and 83° in the quinary system which we have just considered at 25°. The results are very complicated owing to the large number of double salts which exist in the system and the large number of transition points which occur within this temperature range; an exhaustive discussion would occupy a book in itself, and the reader must consult van't Hoff's original publications for further information.

CHAPTER V

GRAPHICAL METHODS. THE PHASE REACTIONS IN EQUILIBRIUM AT THE INVARIANT POINT

§ 83. WE have often seen in the foregoing chapters that the reactions which occur when heat is added to, or abstracted from, a heterogeneous system in invariant equilibrium, depend, in any particular case, upon the relations existing between the compositions of the various phases which participate in the equilibrium. As a simple example, we refer to the invariant equilibrium discussed in §§ 16, 17, 18—that which occurs when an anhydrous salt S and its hydrate H are both in equilibrium with a saturated solution in the binary system W–S. The composition of this saturated solution will generally be expressed in terms of the two components W and S; it may or may not be possible to express its composition in positive terms of H and S, the two solids with which the liquid is in equilibrium. Let us suppose that the hydrate H is a monohydrate of the formula $S.H_2O$, and that the composition of the invariant solution, given in molecular percentages, is

$$x \text{ Moles } S, (100 - x) \text{ Moles } H_2O.$$

We can express the $(100 - x)$ moles of water as $(100 - x)$ moles of the hydrate $S.H_2O$, thus accounting also for $(100 - x)$ moles of the anhydrous salt S, and still leaving $x - (100 - x)$ or $2x - 100$ moles to be represented:

$$(2x - 100) \text{ Moles } S, (100 - x) \text{ Moles } S.H_2O.$$

The quantity $(2x - 100)$ may be positive or negative; *i.e.*, it may be possible to express the composition of the liquid in positive terms of S and $S.H_2O$, or it may be necessary to use a negative value for the concentration of S. The quantity

$(2x - 100)$ will be positive if x is greater than 50, or, in other words, if the molecular percentage of anhydrous salt in the invariant solution is greater than the molecular percentage of salt in the monohydrate. In this case, the separation or dissolution of both anhydrous and hydrated salt in the proportion of $(2x - 100)$ moles of S to $(100 - x)$ moles of $S.H_2O$ will clearly leave the composition of the liquid unaltered; these are, therefore, the phase reactions which must occur when heat is added to, or removed from, the invariant system in equilibrium.

On the other hand, the quantity $(2x - 100)$ will be negative if x is less than 50; let us then denote it by $-y$; the composition of the invariant liquid must now be written:

$$-y \text{ Moles } S,\ (100 - x) \text{ Moles } S.H_2O.$$

If, by the separation of the hydrate, the $(100 - x)$ Moles which are contained by the solution are reduced, for example, to $\frac{1}{2}(100 - x)$ Moles, then the composition of the liquid will remain constant only if the $-y$ moles of S are changed to $-\frac{1}{2}y$ moles; this can only result from the *dissolution* of $+\frac{1}{2}y$ moles of the anhydrous salt, and the phase reactions must in this case consist of the separation of the hydrate and the simultaneous dissolution of anhydrous salt, or the reverse reaction.

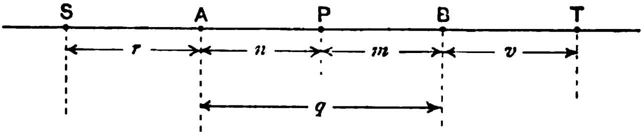

FIG. 157.

Other examples in which the phase reactions occurring at an invariant point—and therefore the polythermal and isothermal types—are dependent upon the compositions of the phases have been noticed in §§ 44 and 58. If these compositions are given in a particular case, the problem of determining the phase reactions which occur is purely mathematical, and it can be solved most readily by the graphical methods which we shall describe in this chapter.

§ 84. Let us suppose that the two points A and B of Fig. 157 represent the compositions of two phases. We have shown in an earlier chapter (§ 23) that, if these are ternary phases the compositions of which are defined by the positions of the points in an equilateral triangle, the composition of a third phase (or complex) formed by mixing these two in a particular proportion is represented by a certain point which lies on the straight line AB between the two points A and B; the composition of this third phase is represented, namely, by a point which divides the line AB into two sections the lengths of which bear to each other the same proportion as do the weights of the two phases A and B which have formed the mixture. The point P of Fig. 157 represents, for example, a mixture of the phase A with the phase B in the proportion by weight of m to n, where the lengths BP, PA are equal to m and n respectively. It is important to notice that the weight of the phase A contained by the mixture P is proportional to the length of that section (BP) of the line AB which lies further from the point A; and that the weight of the phase B is proportional to the length of that section (PA) which lies further from the point B.

This is a purely mathematical deduction, and it can be shown, by geometrical methods, to be independent of the number of components which are assumed for the phases A and B, and of the axes by means of which the positions of the points A and B are defined. It is true whether the phases are binary, ternary, quaternary, etc., and whether their compositions are defined by reference to the sides of a rectangle or of a triangle (equilateral or irregular), or to the faces of a space figure. The point P of Fig. 157 represents, in all of these cases, a mixture of the two phases A and B, the amount of either phase contained in the mixture being proportional to that section of the line AB which lies further from the point representing the phase considered. We can express these conclusions by the following equation:

$$mA + nB = (m + n)P,$$

which must be read: The mixture of m parts by weight of the phase the composition of which is represented by A with n parts by weight of the phase the composition of which is represented by B results in the formation of $(m + n)$ parts by weight of the phase the composition of which is represented by P. When the point P approaches indefinitely close to A, the length m becomes very large compared with n, and the proportion m/n ultimately becomes infinitely large when P coincides with A. When the point P approaches indefinitely close to B, the length m becomes very small compared with n, and the proportion m/n ultimately becomes infinitely small when P coincides with B. Between these two limiting positions of the point P, the fraction m/n assumes all possible positive values, from 0 to $+\infty$; all possible phases or complexes which can result from the mixture of the phases A and B are, therefore, represented by points lying between A and B on the straight line AB.

Let us now consider the relation which exists between the compositions of the phases A and B, and that of a phase represented by the point S, which lies on the straight line AB, but not between A and B. Since the point A now lies between S and B, the phase the composition of which is represented by A can, in accordance with our previous conclusion, be formed by mixing the two phases the compositions of which are represented by S and B. We can write

$$qS + rB = (q + r)A,$$

where the lengths BA, AS are equal to q and r respectively. Hence

$$qS = (q + r)A - rB.$$

We see, therefore, that the phase S cannot be considered as a mixture of *positive* amounts of the two phases A and B. It can never actually result from a simple physical mixture of A and B, though it may be considered mathematically as a mixture of these two in a *negative* proportion. This proportion is

$$-\frac{q+r}{r}, \text{ or } -\frac{q}{r} - 1.$$

When S lies very close to A, the length r is very small compared with q; the value of the fraction $-q/r - 1$ is negative and in this limiting case infinitely large. If S lies far from A in the direction B to A, the length r is very large compared with q; the fraction $-q/r - 1$ is, in this limiting case, equal to -1. Thus, as the point S moves from A to an infinitely remote distance along the line, in the direction B to A, it will represent successively the compositions of all phases which can be considered mathematically as containing the two phases in negative proportions between $-\infty$ and -1.

The composition of the phase represented by the point T, which lies on the opposite side of the length AB, can similarly be expressed in terms of those represented by A and B. Since now the point B lies between A and T, we have

$$qT + vA = (q + v)B$$

or

$$qT = (q + v)B - vA,$$

where the length BT is equal to v. The proportion of the two phases A and B contained in the phase T is, therefore, again negative, and equal to

$$-\frac{v}{q + v}.$$

When T coincides with B, v is equal to zero, and the fraction $-\frac{v}{q+v}$ is also equal to zero. When T lies infinitely far from B in the direction A to B, q is infinitely small compared with v, and the value of the fraction is -1. If we include the case represented by the point S and that represented by the point T in one statement, we can say, therefore, that points which lie on the line AB but not between A and B, represent the compositions of phases which can be considered mathematically as mixtures of the two phases A and B in all possible negative proportions, from $-\infty$ to 0 (from $-\infty$ to -1 on the side remote from B, and from -1 to 0 on the side remote from A).

Every point on the line AB, produced indefinitely at both ends, represents, then, a phase or complex the total composition of which can be expressed mathematically in terms of the compositions of the two phases A and B. If this third phase is represented by a point between A and B, its composition can be expressed in positive terms of these two. Physically, this means that the third phase results from a mixture of the phases A and B. If, on the other hand, the third phase is represented by a point outside the length AB, its composition cannot be expressed in positive terms of the other two, and it cannot be obtained by a simple physical mixture of the phases A and B.

We will now suppose that the points H and S of Fig. 158

represent the compositions of two solid phases which, under certain conditions, can be in invariant equilibrium with a binary liquid phase, and we will suppose, in the first place, that the composition of this liquid phase is represented by a point L_1 which lies between H and S. Now the point L_1 represents, as we have seen, a phase the composition of which can be expressed in terms of positive quantities of the two phases H and S. It follows that the composition of the liquid phase L_1 can be maintained constant by the separation or dissolution of the two solid phases H and S, in a definite proportion: namely, the proportion SL_1/L_1H, in which the phase L_1 contains the two phases H and S, when its composition is expressed in terms of these. The phase reactions which occur when heat is added to, or abstracted from, the invariant system in equilibrium are, therefore, the following:

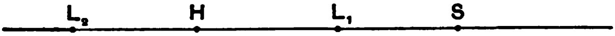

FIG. 158.

$$H + S \rightleftarrows L_1.$$

The upper arrow of the equilibrium sign will again be used to show the reaction which occurs when heat is added to the invariant system; the lower arrow, that which occurs when heat is abstracted from the system. On the addition of heat, the following reaction will occur, then, at constant temperature:

$$H + S \rightarrow L_1.$$

This will result eventually in the disappearance of one of the solid phases H or S, and the formation of one of the following monovariant systems:

S + Liquid.
H + Liquid.

These systems are stable, therefore, at temperatures above the invariant temperature. On the removal of heat from the invariant system, the following reaction will occur at constant temperature:

$$L_1 \rightarrow H + S.$$

This reaction will lead ultimately to the total disappearance of the liquid phase, and the formation of the following monovariant system, which is stable at temperatures below that of the invariant equilibrium :

$$H + S.$$

We shall represent the conditions of equilibrium which exist at, and in the neighbourhood of, the invariant temperature by the notation

$$H + S \rightleftarrows L_1$$
$$H + S \left| \begin{array}{l} S + \text{Liquid} \\ H + \text{Liquid.} \end{array} \right.$$

Here, the monovariant systems which are stable immediately above and immediately below the invariant temperature are written beneath the phase reactions which are in equilibrium at the invariant temperature itself; monovariant systems stable at lower temperatures are written to the left of the upright line, those stable at higher temperatures to the right of that line. Since the only monovariant system to the left of the upright line, in the case we have considered, is the completely solid system $H + S$, it is clear that the invariant point is a lower temperature limit to the existence of the liquid phase; we have already described an invariant point of this nature as a eutectic point.

We will next suppose that the composition of the liquid phase which is in equilibrium with the two solid phases H and S is represented by the point L_2 of Fig. 158. This point lies outside the length HS, and the composition of the liquid phase cannot, therefore, be expressed in positive terms of the two solids. The point H lies, however, between the two points L_2 and S, and the composition of the solid phase H can, therefore, be expressed in terms of positive quantities of the liquid phase L_2 and the second solid phase S. In other words, the solid phase H can be formed by the union of the liquid phase L_2 with the solid phase S, in a definite proportion, namely, the proportion SH/HL_2; this reaction will only affect the weights of the three phases in equilibrium, and it will leave their compositions unaltered. Similarly, the solid phase H may break down into the liquid phase L_2 and the solid phase S, without altering the composition of any phase. The equilibria existing at, and in the neighbourhood of, the invariant temperature are, therefore,

$$H \rightleftarrows S + L_2.$$

$$\begin{array}{l|l} H + \text{Liquid} & \\ & S + \text{Liquid.} \\ H + S & \end{array}$$

Among the monovariant systems which are stable below the invariant temperature we find the system formed by the solid phase H in equilibrium with a liquid phase. The invariant point does not mark, in this case, a lower temperature limit to the existence of the liquid phase; we have described an invariant point of this kind as a transition point.

§ 85. We will suppose that the three points, A, B, and C of Fig. 159 represent the compositions of any three phases. We shall prove that the composition of a fourth phase, formed by mixing these three, is represented by a point within the triangle ABC.

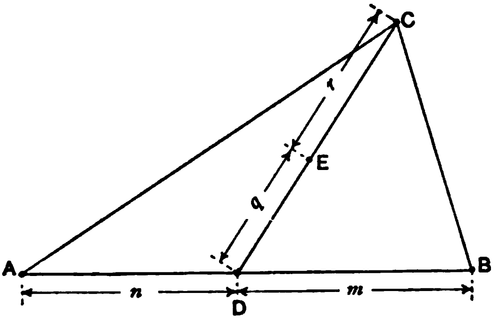

FIG. 159.

The point D (Fig. 159) represents, as we have seen in the previous paragraph, a phase or complex which can be formed by mixing the two phases A and B in the proportion m/n. Further, a point E, on the line CD, represents a mixture of the two phases C and D in the proportion q/r. If the point E moves along the line CD from C to D, the proportion q/r will assume successively all possible positive values, and points on this line represent, therefore, all possible mixtures of the three phases A, B, and C which contain A and B in the fixed proportion m/n. If, now, the point D moves along the line AB from A to B, the fraction m/n will assume successively all possible positive values, and the line CD will generate the triangular area ABC; points in this area give, therefore, the compositions of all phases and complexes which can be formed by mixing the three phases A, B, and C in any positive proportion.

In perfect analogy to the deductions which dealt with the mixtures of two phases, it will be found that any point in the plane of the triangle ABC, but lying outside this triangle, represents a phase or complex the composition of which can still be expressed in terms of the phases A, B, and C, if we admit the use of negative concentration values. Two cases must, however, be distinguished. We will consider first the case represented in Fig. 160. The composition of the phase represented by the point F in this figure cannot be expressed in positive terms of the phases A, B, and C, since the point F does not lie within the triangle ABC. By joining FA and FC, we see, however, that the composition of the phase B can be expressed in positive terms of the phases F, A, and C, since the point B lies within the triangle FAC. We can express this fact by the following equation:

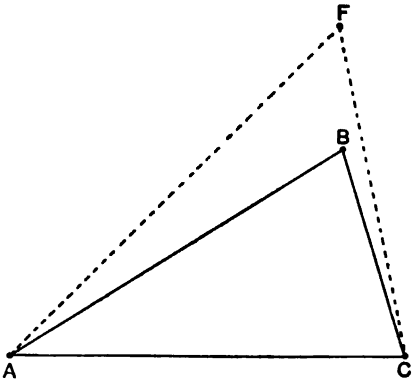

FIG. 160.

$$B = pF + qA + rC,$$

where p, q, and r are positive numbers determined by the position of the point B in the triangle FAC. We then have the following relation, which gives the composition of the phase F in terms of the phases A, B, and C:

$$pF = B - qA - rC.$$

We see that a phase such as F can never result from a simple physical mixture of the phases A, B, and C. Mathematically, it can be considered, however, as a mixture of these three in which the concentrations of *two*, in this case A and C, possess negative values.

The second case is that of a phase the composition of which is represented by a point such as G in Fig. 161. This point also lies outside the triangle ABC, and the composition of the corresponding phase cannot, therefore, be expressed in positive terms of the phases A, B, and C. At the same time, it is impossible, by joining the points representing any three of the phases, to construct a triangle which shall include the fourth point, as we did in the previous case. The present case can only arise when the line which joins the points representing two of the phases intersects the line which joins the points

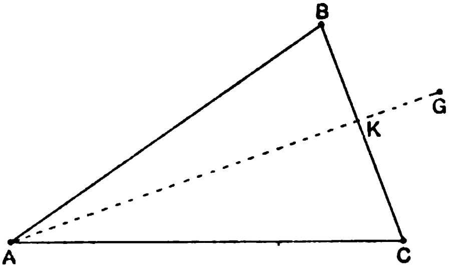

FIG. 161.

representing the other two phases. Thus, in Fig. 161 the line GA intersects the line BC in the point K. This point of intersection represents a phase the composition of which can be expressed in two ways. Since the point K lies on the line GA, we can express the composition of the phase K in positive terms of the phases A and G, thus :

$$K = pA + qG,$$

where p and q are positive numbers determined by the position of the point K on the line GA. Since K lies also on the line BC, we can express the composition of the phase K in positive terms of the phases B and C, thus

$$K = rB + sC,$$

where r and s are positive numbers determined by the position of the point K on the line BC. These two expressions, both giving the composition of the phase K, must be identical, and we have, therefore, the following equation which relates the compositions of the four phases A, B, C, and G:

$$pA + qG = rB + sC$$

or

$$qG = rB + sC - pA.$$

Thus, the phase represented by the point G can still be regarded mathematically as a mixture of the phases A, B, and C, if we admit a negative value for the concentration of *one* of these phases in the mixture—in this case, the phase A.

We will summarise these deductions.

Every point in the plane containing the triangle ABC can be considered mathematically as representing the composition

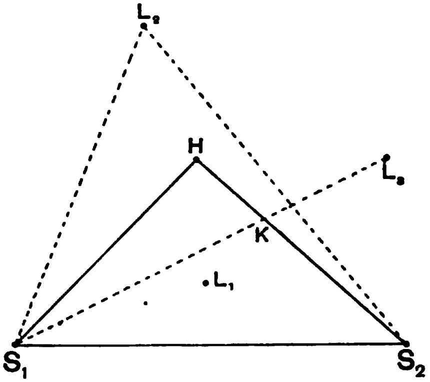

FIG. 162.

of a mixture of the three phases denoted by A, B, and C. Points within the triangle ABC represent mixtures of the three in all possible positive proportions, and are, therefore, to be considered as giving the compositions of all possible physical mixtures of the phases A, B, and C. Points outside the triangle ABC represent mixtures in which the concentration of one, or of two, of the phases A, B, C is negative; a particular example of this case is afforded by a point G, which is so situated with respect to the triangle ABC that the line AG intersects the line BC; the relation which then exists between the compositions of the four phases represented by the points A, B, C, and G is of the form

$$pA + qG = rB + sC,$$

where p, q, r, and s are all positive numbers.

We will suppose that the three points S_1, S_2, and H of Fig. 162

represent the compositions of three solid phases which are in invariant equilibrium with the ternary liquid the composition of which is represented by the point L_1. Since the point L_1 lies inside the triangle HS_1S_2, the composition of the liquid phase can be expressed in positive terms of the three solids. The compositions of all phases can, therefore, be kept constant by the separation or dissolution of the three solids in some definite proportion, namely, the proportion in which they are contained by the liquid phase when its composition is expressed in terms of them. The equilibria which exist at, and in the neighbourhood of, the invariant temperature are, therefore, the following:

$$H + S_1 + S_2 \rightleftarrows L_1$$

$$\begin{array}{l|l} & H + S_1 + \text{Liquid} \\ H + S_1 + S_2 & H + S_2 + \text{Liquid} \\ & S_1 + S_2 + \text{Liquid} \end{array}$$

Since the only monovariant system which can exist below the invariant temperature is the completely solid system

$$H + S_1 + S_2,$$

this case represents the relations which exist at a ternary eutectic point.

If now the composition of the liquid phase which is in invariant equilibrium with the three solid phases H, S_1, S_2 is represented by the point L_2, it can no longer be expressed in positive terms of these solid phases. The composition of the solid phase H can, however, be expressed in positive terms of the liquid phase and the two solid phases S_1 and S_2, since the point H lies within the triangle $L_2S_1S_2$. The compositions of phases can, therefore, be maintained constant by the decomposition of the solid phase H into the liquid phase and the two solid phases S_1 and S_2, or by the union of these to form the solid phase H; in either of these cases, the proportions in which the three phases L_2, S_1, and S_2 take part in the reaction must be the same as that in which they are contained by H when its composition is expressed in terms of them.

The equilibria are

$$H \rightleftarrows S_1 + S_2 + L_2$$

$$\begin{array}{l|l} H + S_1 + \text{Liquid} & \\ H + S_2 + \text{Liquid} & S_1 + S_2 + \text{Liquid} \\ H + S_1 + S_2 & \end{array}$$

The case here described in clearly that of a ternary transition point, since the liquid phase can exist at temperatures below the invariant temperature.

Finally, let us suppose that the composition of the liquid phase in equilibrium with the three solids is represented by the point L_3. In this case, there exists no one phase the composition of which can be expressed in positive terms of the other three. The composition of a complex of the two phases H and S_2 in the definite proportion S_2K/KH, represented by the point K, can, however, be expressed in positive terms of a certain complex of the two phases S_1 and L_3; the complex which contains the two phases in the proportion L_3K/KS_1. The transformation of the one phase complex into the other will leave, therefore, the compositions of phases unaltered; the equilibria at, and in the neighbourhood of, the invariant point are

$$H + S_2 \rightleftarrows S_1 + L_3$$

$$\begin{array}{l|l} H + S_2 + \text{Liquid} & H + S_1 + \text{Liquid} \\ H + S_2 + S_1 & S_2 + S_1 + \text{Liquid} \end{array}$$

Here again the case is that of a ternary transition point.

§ 86. We defined a eutectic point in § 17 as an invariant point which marked a lower temperature limit to the existence of the liquid phase; a transition point as an invariant point which was not so characterised. We have now seen that a eutectic point occurs when the composition of the invariant liquid phase can be expressed in positive terms of the solids with which it is in equilibrium; a transition point, when the composition of the invariant liquid phase cannot be so expressed.

If the composition of a certain phase can be expressed in positive terms of a number of other phases, the given phase is said to be *congruent* with respect to these. If the composition of a phase can be expressed in terms of a number of other phases only by admitting negative terms, the given phase is said to be *incongruent* with respect to these. Thus, at a eutectic point, the invariant solution is congruent with respect to the solid phases with which it is in equilibrium. It is therefore said to be *congruently saturated*. At a transition point, the invariant solution is incongruent with respect to the solid phases with which it is in equilibrium. It is said to be *incongruently saturated.*[1]

The terms eutectic point and transition point are reserved for the characterisation of system invariant points. We may also classify isothermal invariant points according to whether they represent congruently or incongruently saturated solutions, and the distinction between these two classes is fundamentally the same as that between eutectic and transition points. It will not, however, be generally possible to express the composition of an isothermal invariant solution either in positive or in negative terms of those solids *alone* with which it is in equilibrium. The ternary isothermal invariant solution is, for example, in equilibrium with two solid phases only, and these will not suffice to express the composition of the solution. A third phase must be arbitrarily chosen for this purpose. Let us consider the invariant point C in the ternary isotherm of Fig. 21. This point represents a solution in equilibrium with the simple salt S_1 and the anhydrous double salt denoted by the point D. It is clearly impossible to express the composition of the solution C in terms of the two solid phases S_1 and D alone; we have shown in § 84 that the only phases the compositions of which can be so expressed are those which are represented by points on the line S_1D. In addition to the two solid phases S_1 and D, we shall choose water as the third phase in terms of which the composition of the solution is to be expressed. An isothermal invariant solution will then be described as congruently or incongruently saturated when it is congruent or incongruent with respect to *water and* the solid phases with which it is in equilibrium. The point C lies outside the triangle WS_1D, and it is, therefore, impossible to express the composition of the solution C in positive terms of water and the two solids S_1 and D, with which it is in equilibrium; the solution is incongruent with respect to these phases, and is therefore described as incongruently saturated. The line S_1C of Fig. 21 intersects the line DW, and a certain complex (J) of the solution C with the salt S_1 can therefore be expressed mathematically as a complex of water and the double salt D:

$$S_1 + \text{Solution } C = D + W.$$

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[1] We have already introduced these terms (§ 30), but we are now able to give them more precise definition.

It must be carefully observed that the above relation is purely mathematical, and does not represent reactions in equilibrium at the isothermal invariant point C; the third phase W is, in this case, arbitrarily chosen, and does not actually partake in the equilibrium. If, however, water is withdrawn from the invariant system at constant temperature, the equilibrium will be disturbed, since the water content of the liquid phase will be diminished. A phase reaction must, therefore, immediately set in which, whilst removing water, retains the original invariant composition of the solution. This reaction is:

$$S_1 + \text{Solution } C \longrightarrow D + W \text{ (removed)};$$

it alters the proportions which the weights of the separate phases bear to each other, but does not alter their actual compositions. The effect of the evaporation of water from the isothermal invariant system in equilibrium at the point C of Fig. 21 is, therefore, to cause the dissolution of the salt S_1 and the separation of the salt D; we have already deduced this behaviour in § 30.

As another example, we will consider the ternary system represented in Fig. 23. At the temperature of this isotherm, the hydrate H_1, which is the stable solid phase in the binary system W–S_1, suffers dehydration by certain ternary solutions; the isothermal invariant point E represents the solution in equilibrium with the hydrate, denoted by the point H_1, and the anhydrous salt, denoted by the point S_1. Here, again, it is clearly impossible to express the composition of the solution E in terms of the two solid phases H_1 and S_1 alone. Nor can we choose water as the third phase for this purpose, since the point W itself lies on the straight line H_1S_1. The solution E cannot, therefore, be described either as congruently or as incongruently saturated, in the sense of our definition of these terms; the composition of the solution E cannot be expressed either in positive or negative terms of water and the solids with which it is in equilibrium. Since the point E lies outside the triangle $S_1H_1S_2$, we may say, however, that the solution E is incongruent with respect to the three phases S_1, H_1, and S_2. The line S_2H_1 intersects the line S_1E, and the relation between the composition of the four phases is, therefore, of the form:

$$S_2 + H_1 = S_1 + \text{Solution } E.$$

This is, again, a mathematical relation, and not a phase equilibrium; the salt S_2 does not actually form one of the solid phases in equilibrium with the invariant solution E. If the salt S_2 is added to this invariant system, it must, on the contrary, dissolve, since the solution is not saturated with respect to S_2. This will, however, alter the composition of the liquid phase, and a phase reaction must set in which, whilst dissolving S_2, retains the invariant composition of the solution. This reaction is:

$$S_2 \text{ (Dissolved)} + H_1 \rightarrow S_1 + \text{Solution } E.$$

The added salt S_2 dissolves, together with some of the hydrate present in equilibrium with the solution, and the anhydrous salt S_1 separates, a behaviour which we had already predicted in § 32.

§ 87. In order to illustrate further the principles developed in the foregoing paragraphs, we shall now reconsider the polytherms in the binary system W–S_1, and the ternary system W–S_1–S_2, for the case in which a salt hydrate H_1 can occur as a solid phase.

The polythermal relations in the ternary system can be represented, completely by means of a space figure referred to a triangular prism (§ 36), incompletely by means of a plane projection of that figure upon the triangular base of the prism (§ 37) or upon the rectangular face TS_1S_2 (Jänecke's method, § 38). Of the two plane representations, the first is incomplete because the temperature corresponding with a given point in the figure is not expressed by the figure, whilst the second, although it gives direct expression to the temperature, does not represent the water content of solutions. In Chapter II, we have always used Jänecke's method for representing the polythermal conditions of ternary equilibria because it readily lends itself to the deduction of isothermal types. In this paragraph we shall use the projection upon the base of the prism.

The polythermal conditions of equilibrium in the ternary system W–S_1–S_2, when the simple salt hydrate H_1 can occur as a solid phase, are represented within the triangle WS_1S_2, in Figs. 163 and 164. The binary system W–S_1 is represented on the side WS_1 of the triangle, and, since the hydrate occurs as a solid phase in this system, the latter possesses two system invariant points, *D* and *E*. At the temperature corresponding with the point *D*, an invariant liquid is in equilibrium with the two solid phases H_1+ Ice, and at that corresponding with the point *E*, an invariant liquid is in equilibrium with the two solid phases H_1+S_1. In both Fig. 163 and Fig. 164 the point *D* lies between the points H_1 and *W*, which represent, respectively, the hydrate H_1 and ice; these are the solid phases in equilibrium with the solution *D*, the composition of which can, therefore, be expressed in terms of them. The equilibria which exist at, and in the neighbourhood of, this invariant temperature are

$$H_1 + \text{Ice} \rightleftarrows \text{Solution } D$$

$$H_1 + \text{Ice} \left| \begin{array}{l} \text{Ice} + \text{Solution} \\ H_1 + \text{Solution.} \end{array} \right.$$

The point *D* represents a congruently saturated solution, and it is, therefore, a binary eutectic point. The two monovariant systems Ice + Solution and H_1+ Solution are both stable at temperatures above that of the invariant point, and the two saturation curves which diverge from the point *D* (those of ice and H_1) both do so in the direction of rising temperature. These two binary saturation curves are contained by the side WS_1, and they are represented by the parts *DW* and *DE*; the direction of temperature change on these curves is shown by the arrow-heads, which point in the direction of rising temperature, and which are directed, therefore, both along *DW* and *DE*, away from the point *D*.

The binary eutectic point *D* forms the starting point of a ternary saturation curve *DG*, that of H_1+ Ice. Every point on this curve represents a ternary solution which is in equilibrium at a definite, though unexpressed, temperature with the two solid phases H_1+ Ice; the curve may be considered as the locus, with varying temperature, of the isothermal invariant point which represents a ternary solution in equilibrium with these two phases.

The curve *DG* ends in a ternary invariant point *G*, at which the salt S_2 appears as a third solid phase. The point *G* represents an invariant solution which is in equilibrium with the three solid phases denoted by the points H_1, *W*, and S_2, and, since it lies within the triangle H_1WS_2, the composition of the solution G can be expressed in positive terms of the solids H_1, ice, and S_2, with which it is in equilibrium; the equilibria at, and in the neighbourhood of, this invariant point are:

$$\text{Ice} + H_1 + S_2 \rightleftarrows \text{Solution } G.$$

$$\text{Ice} + H_1 + S_2 \left| \begin{array}{l} \text{Ice} + H_1 + \text{Solution} \\ \text{Ice} + S_2 + \text{Solution} \\ \text{H}_1 + S_2 + \text{Solution} \end{array} \right.$$

The solution G is congruently saturated, and the point G is a ternary eutectic point. The three monovariant systems Ice + H_1 + Solution, Ice + S_2 + Solution, $\text{H}_1 + S_2$ + Solution are all stable at temperatures above that of the point G. The three corresponding saturation curves GD, GC, GM diverge from the point G in the direction of rising temperature; the arrow-heads on these curves are all directed away from G, thus characterising it as a temperature minimum.

The curve GD is the ternary saturation curve of Ice + H_1, which we have already discussed; it ends in the binary eutectic point D, at which ice and the hydrate are in equilibrium with a binary invariant solution.

The curve GC is the saturation curve of Ice + S_2, and it also ends in a binary invariant point; the point C, at which Ice + S_2 are in equilibrium with an invariant liquid in the system W–S_2. This system is represented on the side WS_2 of the triangle, and it is of the simplest type, since the only solid phases which can occur are the solid components ice and S_2. The invariant point C, which represents the solution in equilibrium with both these solids, is clearly a eutectic point:

$$\text{Ice} + S_2 \rightleftarrows \text{Solution } C$$

$$\text{Ice} + S_2 \left| \begin{array}{l} \text{Ice} + \text{Solution} \\ S_2 + \text{Solution} \end{array} \right.$$

The two corresponding binary saturation curves (of ice and S_2) are contained by the side WS_2, and are represented by the parts CW and CS_2; the arrow-heads on these curves are directed away from the point C.

The curve GM—the third which diverges from the ternary eutectic point G—is the ternary saturation curve of $H_1 + S_2$; before we discuss this curve we must consider the second invariant point E, in the binary system W–S_1—that which represents a solution in equilibrium with the two solid phases H_1 and S_1; and here we must distinguish between the two cases represented in Figs. 163 and 164. The point E in Fig. 163 lies between the two points H_1 and S_1, which represent the solid phases in equilibrium with the solution E. The composition of this solution can, therefore, be expressed in positive terms of the solids H_1 and S_1, and the equilibria existing at, and in the neighbourhood of, the invariant point are

$$H_1 + S_1 \rightleftarrows \text{Solution } E$$
$$H_1 + S_1 \left| \begin{array}{l} H_1 + \text{Solution} \\ S_1 + \text{Solution} \end{array} \right.$$

The point E is, in this case, a eutectic point, and the binary system W–S_1 is of the type which we discussed in detail in § 16. The two saturation curves which diverge from the point E are represented by the parts ED and ES_1 of the side of the triangle, and the direction of temperature change is shown by the arrowheads. We have seen already that the other extremity of the binary saturation curve ED, of the hydrate, is formed by the eutectic point D. This curve diverges from both eutectic points E and D in the direction of rising temperature, as the converging arrow-heads show; it must, therefore, attain a temperature maximum. We have shown in § 16 that this maximum occurs at the melting point of the hydrate, where the liquid phase has the same composition as the solid hydrate. The point H_1 itself represents, therefore, the point of maximum temperature on the saturation curve ED of Fig. 163.

In Fig. 164 the point E does not lie between the two points H_1 and S_1, which represent the compositions of the solid phases in equilibrium with the invariant solution; this solution is, in other words, incongruently saturated. Since, however, the point H_1 lies between the points S_1 and E, the composition of the hydrate can be expressed in positive terms of the anhydrous salt and the invariant solution. The equilibria at, and in the neighbourhood of, this invariant point are

$$\mathrm{H}_1 \rightleftarrows \mathrm{S}_1 + \text{Solution}$$
$$\left. \begin{array}{l} H_1 + \text{Solution} \\ H_1 + S_1 \end{array} \right| \mathrm{S}_1 + \text{Solution}$$

The point E is, in this figure, a transition point, and the binary system W–S_1 is of the type which we discussed in detail in § 17. The monovariant system S_1+ Solution is stable at temperatures above that of the invariant point; the corresponding saturation curve ES_1 diverges from the point E in the direction of rising temperature. The monovariant system H_1+ Solution is stable at temperatures below that of the invariant point, and the corresponding saturation curve ED, of H_1, diverges from the point E in the direction of falling temperature; since this curve diverges from the eutectic point D in the direction of rising temperature, it does not pass through a temperature maximum.

We will consider first the conditions of equilibrium represented by Fig. 163. The point E is here a binary eutectic point representing the invariant solution in equilibrium with the two solids H_1 and S_1, and it forms the starting point of a ternary saturation curve: EM that of H_1+S_1. This curve ends in the ternary invariant point M, a point which represents a ternary solution in equilibrium, not only with H_1+S_1, but also with the third solid phase S_2. The point M lies within the triangle the vertices of which, H_1, S_1, and S_2, represent the three solid phases in equilibrium with the invariant solution M. The equilibria at, and in the neighbourhood of, the invariant temperature are, therefore,

$$H_1+S_1+S_2 \rightleftarrows \text{Solution } M.$$

$$H_1+S_1+S_2 \left| \begin{array}{l} H_1+S_1+\text{Solution} \\ S_1+S_2+\text{Solution} \\ H_1+S_2+\text{Solution} \end{array} \right.$$

The point M is a second ternary eutectic point, and all saturation curves which diverge from it do so in the direction of rising temperature, as the arrow-heads show in the figure.

The curve ME is the saturation curve of H_1+S_1, which ends in the binary eutectic point E. The curve MF is the saturation curve of S_1+S_2, and it also ends in a binary eutectic point: namely, the invariant point F in the system S_1–S_2, which is of the same simple type as the system W–S_2.

The curve MG is the saturation curve of H_1+S_2, and we have seen earlier in this paragraph that its other extremity is formed by the ternary eutectic point G; from both eutectic points M and G it diverges in the direction of rising temperature, and it must, therefore, pass through a temperature maximum between the two.

The ternary saturation curve *MG*, of $H_1 + S_2$, can be compared with the binary saturation curve *ED*, of H_1. Both curves are terminated at each end by eutectic points, and both pass through a temperature maximum; this is shown graphically by the fact that, on each curve, the arrow-heads are directed towards each other.

Let us consider the ternary saturated solutions which contain the two components *W* and S_1 in the same proportion as that in which they unite to form the hydrate H_1. The compositions of these solutions can clearly be expressed in terms of the hydrate H_1 and the salt S_2, and they must, therefore, be represented by points on the straight line H_1S_2 of Fig. 163. The only ternary saturation surfaces which this line traverses are those of H_1 and S_2, and the only ternary saturation curve which it intersects is *MG*, that of $H_1 + S_2$. The only solid phases which can be in equilibrium with solutions the compositions of which can be expressed in terms of H_1 and S_2 alone are, therefore, H_1 and S_2. The system H_1–S_2 is, in other words, a true binary system, and it is represented on the straight line H_1S_2, just as the binary system *W*–S_2 is represented on the line WS_2. That part (KS_2) of the line WS_2 which lies on the ternary saturation surface of S_2 represents the binary saturation curve of S_2 in the system H_1–S_2; and the part KH_1, which lies on the saturation surface of H_1, represents the binary saturation curve of H_1, in this system. The point *K* represents an invariant solution in the binary system H_1–S_2, namely the invariant solution which is in equilibrium with the two solid phases $H_1 + S_2$. From the position of the point *K* on the line H_1S_2, and between the points H_1 and S_2, it follows that the equilibria existing at, and in the neighbourhood of, this binary invariant point are

$$H_1 + S_2 \rightleftarrows \text{Solution } K$$

$$H_1 + S_2 \left| \begin{array}{l} H_1 + \text{Solution} \\ S_2 + \text{Solution} \end{array} \right.$$

The point *K* is a binary eutectic point, and the two saturation curves which diverge from it do so in the direction of rising temperature; this is indicated by the arrow-heads on the lines KH_1 and KS_2, which represent these saturation curves.

It is clear that Fig. 163 is divided by the straight line H_1S_2 into two parts, and these can be considered as giving the polythermal conditions of equilibrium in two independent ternary systems of the simplest type—systems in which only the components appear as solid phases. The polytherm in the system H_1–S_1–S_2 is represented within the triangle $H_1S_1S_2$, and it can be compared with the simple type depicted in Fig. 42 of § 37. It shows three polythermal saturation curves:

ME is the saturation curve of $H_1 + S_1$
MF „ „ „ $S_1 + S_2$
MK „ „ „ $H_1 + S_2$.

The saturation curve *ME*, of $H_1 + S_1$, diverges in the direction of rising temperature from the ternary eutectic point *M*, and reaches its temperature maximum in the binary eutectic point *E*; this latter point represents the binary invariant solution which is also saturated with $H_1 + S_1$. The saturation curve *MF*, of $S_1 + S_2$, diverges in the direction of rising temperature from the ternary eutectic point *M*, and reaches its temperature maximum in the binary eutectic point *F*—a point which represents the binary invariant solution also saturated with $S_1 + S_2$. Similarly, the ternary saturation curve *MK*, of $H_1 + S_2$, must reach its temperature maximum in the point which represents a binary invariant solution saturated with these two solids. This is the point *K*, which we have shown to be the eutectic point in the binary system H_1–S_2.

The polytherm in the system W–H_1–S_2 is represented within the triangle WH_1S_2, and it also shows only three saturation curves. The curve *GD* is the saturation curve of Ice + H_1, and it reaches its temperature maximum in the point *D*, which represents the binary eutectic solution in equilibrium with Ice + H_1. The curve *GC* is the saturation curve of Ice + S_2, and it reaches its temperature maximum at the corresponding binary invariant point *C*. The curve *GK* is the saturation curve of $H_1 + S_2$ in this system; it, like the saturation curve *MK* in the system H_1–S_1–S_2, reaches its temperature maximum at the binary eutectic point *K*.

We saw earlier in this paragraph, when considering the system W–S_1–S_2 as a whole, that the saturation curve *GM*, of $H_1 + S_2$, must pass through a temperature maximum, since it ends, on both sides, in a ternary eutectic point. We have now seen that this point of maximum temperature lies at the intersection K, of the curve, with the straight line H_1S_2. In the same way, for example, the saturation curve MF, of $S_1 + S_2$, reaches its temperature maximum in the point F, where it intersects the straight line S_1S_2; the saturation curve ME, of $H_1 + S_1$, reaches its temperature maximum in the point E, where it intersects the straight line H_1S_1, etc.

We can say, quite generally, that a curve the points of which represent the compositions of ternary solutions in equilibrium with the two solid phases X and Y must attain a temperature maximum at the point where it intersects the straight line XY. The law upon which this graphical deduction is based may be stated: A *ternary polythermal saturation curve* which represents solutions in equilibrium with the two solid phases X and Y reaches its temperature maximum in the point which represents a *binary invariant solution* in equilibrium with the same two solid phases. All binary mixtures of the two phases X and Y, and therefore also the binary invariant solution, must, however, be represented by points on the straight line XY. Hence we arrive at the graphical deduction stated above: the saturation curve of $X + Y$ reaches its temperature maximum on the straight line XY.

We shall now consider the case which is represented in Fig. 164. The point E is here a binary *transition* point; it represents an incongruently saturated invariant solution in equilibrium with the hydrate H_1 and the anhydrous salt S_1. As before, the point E forms the starting point of the ternary saturation curve of $H_1 + S_1$, and this curve ends in the ternary invariant point M, where the second salt S_2 appears as a third solid phase. The point M represents a ternary invariant solution in equilibrium with the three solid phases denoted by the points H_1, S_1, and S_2, but it does not lie within the triangle $H_1S_1S_2$, and the invariant solution is, therefore, incongruently saturated. The line joining the points M and S_1 intersects that which joins the points H_1 and S_2. We have shown in § 85 that, in this case, the composition of a certain phase complex formed by the solution M and the solid S_1 can be expressed in terms of a complex formed by the two solids H_1

and S_2. The phase reactions which occur at, and in the neighbourhood of, the invariant point are

$$H_1 + S_2 \rightleftarrows S_1 + \text{Solution } M$$

$$\begin{array}{r|l} H_1 + S_2 + \text{Solution} & H_1 + S_1 + \text{Solution} \\ H_1 + S_2 + S_1 & S_2 + S_1 + \text{Solution.} \end{array}$$

The monovariant system $H_1 + S_2 +$ Solution is now stable at temperatures below that of the invariant point, and the corresponding saturation curve *MG* (Fig. 164) diverges from the point *M* in the direction of falling temperature. Since it diverges from the eutectic point *G* in the direction of rising temperature, it does not pass through a temperature maximum between these points. This saturation curve must, as we have already seen, attain its temperature maximum at its point of intersection with the straight line H_1S_2. It does not, however, intersect this line in stable regions; a solution which is in equilibrium with $H_1 + S_2$, and the composition of which can be expressed in terms of H_1 and S_2 alone, is represented by the point *K*, in which the metastable prolongation of the saturation curve *GM* intersects the line H_1S_2. This point would be a point of maximum temperature on the saturation curve *GM*, but the system formed by the solution *K* in equilibrium with the two solid phases H_1 and S_2 is, actually, metastable; since the point *K* lies on the saturation surface of S_1, such a solution would be supersaturated with respect to this salt.

The point *M* is a ternary transition point, just as the point *E* is a binary transition point. The binary saturation curve, *DE*, of the hydrate, does not attain its temperature maximum in stable regions, *i.e.*, the hydrate has no stable melting point; in the same way, the ternary saturation curve *GM*, of $H_1 + S_2$, does not attain its temperature maximum in stable regions, *i.e.*, there exists no stable binary invariant system formed by the two solids H_1 and S_2 in equilibrium with a binary solution. It can be seen from Fig. 164 that the system H_1–S_2 does not, in fact, behave as a binary system. The straight line H_1S_2 intersects the saturation surface of S_1, and this salt can, therefore, be in equilibrium with solutions the compositions of which can be expressed in terms of H_1 and S_2 alone; the composition of the anhydrous salt S_1 cannot, however, be so expressed, and the system H_1–S_2 is not binary. The figure is not divided into two simpler ternary polytherms by the line H_1S_2.

§ 88. The two typical ternary polytherms of Figs. 163 and 164 are characterised by the fact that, in the first, the binary invariant point E and the ternary invariant point M are both eutectic points or temperature minima; in the second, both binary and ternary invariant points are transition points. The two polytherms of Figs. 163 and 164 are represented by Jänecke's method in Figs. 165 and 166 respectively. The same lettering has been used, and a comparison will show that Fig. 165 corresponds strictly with Fig. 163, Fig. 166 with Fig. 164. Considering first Fig. 165, we see that the two ternary invariant points G and M are both eutectic points; both points are temperature minima, and all saturation curves which diverge from them do so in the direction of rising temperature. The saturation curve of H_1+S_2, which joins the two ternary eutectic points, passes through a temperature maximum at the point K; we have already seen that this point is a eutectic point in the binary system H_1–S_2. In Fig. 166, the point M is a transition point; it is not a temperature minimum, since the saturation curve of H_1+S_2 diverges from it in the direction of falling temperature, and does not pass through a maximum.

The ternary polytherm which we discussed in § 44 of Chapter II. (*cf.* Fig. 53) was of the type illustrated in Fig. 166. We shall now consider some isothermal types which may be derived from the polytherm of Fig. 165. This figure can be considered as built up from the polytherms in two simpler systems. The invariant point G represents the eutectic solution in equilibrium with the three solid phases, ice, H_1, and S_2. From it, there rise three saturation curves: GD is the saturation curve of Ice $+ H_1$, and it ends at the eutectic point D in the binary system W–S_1; GC is the saturation curve of Ice $+ S_2$ and it ends at the eutectic point C in the binary system W–S_2; GK is the saturation curve of H_1+S_2, and it ends at the point K, which we have seen to be the eutectic point in the binary system H_1–S_2. These three saturation curves can be considered as forming a simple ternary polytherm similar to that shown in Fig. 43; it is the polytherm in the system W–H_1–S_2. Similarly, the invariant point M represents the eutectic solu-

tion in equilibrium with the three solid phases S_1, H_1, and S_2, and the saturation curves which rise from it end at the corresponding binary eutectic points E, K, and F. They form the polytherm in the simple ternary system S_1–H_1–S_2. The isotherms in *each* of these two systems will pass, within different temperature ranges, through the various isothermal types which we have discussed in detail in § 34, and the possible combinations of the separate types in one picture will represent the isothermal relations in the system W–S_1–S_2 for the case here considered.

If we represent the isotherm in the system W–S_1–S_2, within the triangle WS_1S_2 (Fig. 167), that portion of it which lies within the triangle WH_1S_2 will represent the isotherm in the simple ternary system W–H_1–S_2, and that portion which lies within the triangle $S_1H_1S_2$ the isotherm in the simple ternary system S_1–H_1–S_2, at the same temperature. At a temperature T_1, sufficiently low, the constant temperature line in the polytherm (Fig. 165) cuts only the saturation surfaces of H_1 and of S_2, and the saturation curve of H_1+S_2, in the system W–H_1–S_2. The isothermal type is of the simple form shown in Fig. 167. The curves YV and ZV are the isothermal saturation curves of H_1 and S_2, respectively, in the system W–H_1–S_2. All mixtures in the system S_1–H_1–S_2 are, as yet, completely solid, for the constant temperature line in Fig. 165 lies below the eutectic point M of this system; no saturation curves can extend, therefore, into the triangle $S_1H_1S_2$ of the isotherm shown in Fig. 167.

If the temperature is raised to T_2, that of the eutectic point M, one solution can exist in the system H_1–S_1–S_2, namely, the eutectic solution itself. The corresponding isothermal transition form is given by Fig. 168, where the point M represents the eutectic solution saturated with the three solids $H_1+S_1+S_2$, in the system H_1–S_1–S_2; it is the only point in the triangle $H_1S_1S_2$ which represents a saturated solution. The system W–H_1–S_2 still shows the isothermal saturation curves YG and ZG, of H_1 and S_2, given by the intersection of the constant temperature line in the polytherm, with the corresponding saturation surfaces.

At a temperature T_3, slightly above that of the eutectic point M, the constant temperature line of the polytherm cuts all three saturation curves in the system S_1–H_1–S_2, and the isotherm is then given by Fig. 169. The system invariant point *M* in the transition type of Fig. 168 is replaced, at slightly higher temperatures, by three isothermal invariant points—the points *J*, *B*, and *L*, in which the constant temperature line intersects the polythermal saturation curves *ME*, *MF*, and *MK* of Fig. 165. The isothermal type which exists at a temperature immediately above that of a ternary eutectic point has already been deduced in § 34, and illustrated in Fig. 34. A comparison of the isotherm represented within the triangle $S_1H_1S_2$ of Fig. 169, with that represented within the triangle WS_1S_2 of Fig. 34, will show that these two belong to the same isothermal type. The present case is complicated by the fact that the triangle WS_1S_2 of Fig. 169 contains a second isotherm—the isotherm in the system W–H_1–S_2, which is represented within the triangle WH_1S_2. This isotherm belongs to a different type from that shown by the system S_1–H_1–S_2; it belongs to the type represented in Fig. 28 of § 34, and the isotherm in the system W–S_1–S_2, regarded as a whole, is a combination of two simple types. In Fig. 169 there are two isothermal saturation curves of H_1 (*YA* and *LJ*), and two of S_2 (*ZA* and *LB*), namely, one in each of the systems W–H_1–S_2 and S_1–H_1–S_2. Further, there are two isothermal invariant points (*A* and *L*) which both represent solutions in equilibrium with the two solid phases H_1 and S_2, again one in each of the two simpler isotherms. The existence of these two isothermal invariant points is due to the fact that the constant temperature line in the polytherm (Fig. 165) intersects the saturation curve *GKM*, of $H_1 + S_2$, in two points, one on each side of the maximum.

It can be seen from the polytherm that, when the temperature is raised above T_3, the two points *A* and *L* approach one another, and finally coincide in the maximum *K*. We have shown that this point represents the eutectic point in the binary system H_1–S_2. The isothermal transition form at this binary eutectic temperature T_4 is therefore given by Fig. 170. The two isothermal invariant points *A* and *L* of Fig. 169, which represent solutions saturated with $H_1 + S_2$, coincide at the temperature T_4, in the point *K*, on the line H_1S_2. The discontinuity in the saturation curves of H_1 and of S_2, represented by the gap *AL* of Fig. 169, has disappeared, and the two curves touch one another in the point *K*.

At a temperature T_5, slightly above T_4, solid H_1 and solid S_2 cannot exist together in equilibrium with solutions, since the constant temperature line in the polytherm does not now intersect the saturation curve *GKM*, of $H_1 + S_2$. The isothermal type is therefore given by Fig. 171, in which the saturation curves of H_1 and S_2 are entirely separated from each other. Here again, the isotherms in the systems W–H_1–S_2 and H_1–S_1–S_2 show types which have already been deduced for the simple ternary system (Figs. 37 and 32).

The next isothermal transition form occurs at the temperature of the binary eutectic point *E* in Fig. 165. At this temperature the two solids H_1 and S_1 can exist in equilibrium with a solution in the binary system W–S_1. The isothermal invariant point *Q* of Fig. 171, which represents the solution saturated with $H_1 + S_1$, must therefore fall on the line WS_1 at the temperature of the point *E*, and the corresponding isothermal transition form is given by Fig. 172.

At a temperature immediately above that of the point *E*, the two solids H_1 and S_1 cannot exist together in equilibrium with a solution, since a constant temperature line in Fig. 165 no longer intersects the polythermal saturation curve of $H_1 + S_1$. The isothermal type is now given by Fig. 173, in which the saturation curves of H_1 and S_1 are completely separated from each other; this isotherm can again be considered as built up from two simpler types (Figs. 29 and 37).

The isothermal saturation curve of the hydrate is given by a curve *YUX*, surrounding the point H_1, and bounded on each side by the side WS_1.

In order to understand how the saturation curve of the hydrate obtains the form shown by the isothermal type of Fig. 173, we must consider the complete space polytherm, of which Figs. 163 and 165 are plane projections. A part of this space figure, namely, the saturation surface of the hydrate, is represented within the triangular prism of Fig. 174. The ternary saturation surface of the hydrate rises from the two ternary eutectic points *G* and *M*, and it is bounded, in the face of the prism, by the binary saturation curve DH_1E, of the hydrate, in the system W–S_1. This curve passes through a temperature maximum at the point H_1, which represents a liquid phase in equilibrium with the solid hydrate, and of identical composition with it; the temperature corresponding with the point H_1 is, in other words, the melting point of the pure hydrate. This is the highest temperature at which solid hydrate can be in equilibrium with a liquid phase, and the saturation surface of the hydrate, after rising from the eutectic points G and M, reaches its highest point, therefore, at the point H_1, in the face of the prism which bounds the surface. The isotherm at a particular temperature is given by the intersection of a plane parallel to the base of the prism with the various saturation surfaces and curves which form the space figure. Now it is clear from the shape of the saturation surface of the hydrate that, at a temperature slightly below the melting point of the hydrate, a plane parallel to the base will intersect this surface in a curve which extends, without interruption, from one point on the side WS_1 of the triangular section to another point on the same side. The isothermal saturation curve of the hydrate will then have the form shown by the curve YUX in the polytherm of Fig. 174, and in the isotherm of Fig. 173. As the temperature falls, the curve YUX (Fig. 174) will increase in size until the temperature of the point E is reached. A section of the saturation surface at a temperature below this is bounded by the ternary saturation curve EM, which lies within the prism; the isothermal saturation curve of the hydrate will then no longer be bounded on *both* sides by the face WS_1, and, with falling temperature, the isotherm will pass through the series of types which we have already deduced. If, however, the temperature is raised, the curve YUX will diminish in size, the two points Y and X will approach each other, and the saturation curve YUX will disappear entirely when these points coincide in the highest point of the saturation surface. At the melting point of the hydrate, the saturation curve of the hydrate shrinks, therefore, into the point H_1. At still higher temperatures, the two anhydrous salts S_1 and S_2 can alone occur as solid phases, and the isotherm is of the simple type which shows only two saturation curves.

We can now summarise the isothermal types which may occur in the system W–S_1–S_2, in which the hydrate H_1 appears as a solid phase; we assume that the binary solution in equilibrium with $H_1 + S_1$, and the ternary solution in equilibrium with $H_1 + S_1 + S_2$, are both congruently saturated, *i.e.*, the two corresponding system invariant points are eutectic points. The saturation curve of the hydrate appears and disappears in the point H_1, at the melting temperature of the hydrate. At a temperature slightly below this, it is given by a curve surrounding the point H_1, and bounded at each end by the side WS_1 of the triangle (Fig. 173). As the temperature falls, the saturation curve of the hydrate expands, and may intersect first the saturation curve of S_1 (Fig. 171). Later, it may touch and then intersect the saturation curve of S_2 also (Figs. 170 and 169). The two saturation curves, of S_1 and H_1, then become interrupted, and the two systems W–H_1–S_2 and S_1–H_1–S_2 can be considered as entirely independent. The former shows three isothermal invariant points (Fig. 169), which approach one another and finally coincide in the eutectic point M, at the corresponding eutectic temperature (Fig. 168). If the temperature is still further lowered, only completely solid phases or complexes can exist in the system S_1–H_1–S_2, whilst an ice saturation curve must make its appearance in the system W–H_1–S_2 below 0°. This system then passes through identically the same changes of isothermal type as did the other system at higher temperatures, the saturation curves of the three components ice, H_1 and S_2 shrinking finally into the second ternary eutectic point G.

We have not, even now, exhausted all the possibilities, since we have assumed in Fig. 165 that the temperature of the eutectic point K in the binary system H_1–S_2 is lower than that of the eutectic point E in the binary system H_1–S_1. If the contrary is the case, then, as the temperature is lowered below the melting point of the hydrate, the isothermal saturation curve of the hydrate will intersect first the saturation curve of S_2, and afterwards that of S_1; we shall leave the corresponding isothermal types to be deduced by the reader.

§ 89. We will discuss briefly the polythermal relations in the ternary system in which a ternary compound (the hydrated double salt) can exist as a solid phase. We shall not treat this case exhaustively, since the number of different types which may occur is very large.

We will suppose that, within a certain range of temperature, the hydrated double salt D cannot exist in equilibrium with solutions, but that it breaks down at these temperatures, into the two simple salt hydrates H_1 and H_2; within another temperature range, the two simple hydrates cannot both exist in equilibrium with solutions, but unite to form the double salt hydrate. We must then study the invariant phase equilibrium which exists when H_1, H_2, and D are all in stable contact with a saturated solution.

It must always be possible to express the composition of the hydrated double salt in terms of water and the two hydrated simple salts. We can distinguish the three following possibilities.

1. The hydrated double salt may be formed by the direct union of the two simple hydrates, without either absorption or elimination of water. We can then write

$$mH_1+nH_2=D.$$

In this case, the composition of the salt D can be expressed in terms of H_1 and H_2 alone, and the point representing this salt must lie on the line joining H_1 to H_2, as represented in Fig. 175.

2. The formation of the hydrated double salt may require more water than can be supplied by the two hydrates; we can then write

$$pH_1+qH_2+rW=D.$$

In this case, the composition of the double salt can be expressed in positive terms of water and the two hydrates, and the point representing the double salt must lie within the triangle WH_1H_2, as in Fig. 176.

3. The double salt may be formed by the union of the two simple hydrates with the simultaneous elimination of water; we can then write

$$pH_1+qH_2=rD+sW.$$

In this case, the point representing the double salt must be so situated that the line H_1H_2 intersects the line WD, as shown in Fig. 177.

We will limit our discussion to the case represented in Fig. 176 where the hydrated double salt can be formed by the direct union of water and the two simple hydrates. Since,

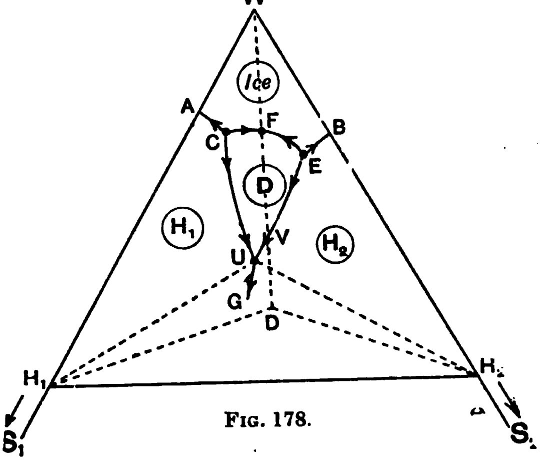
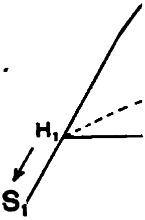


FIG. 178.



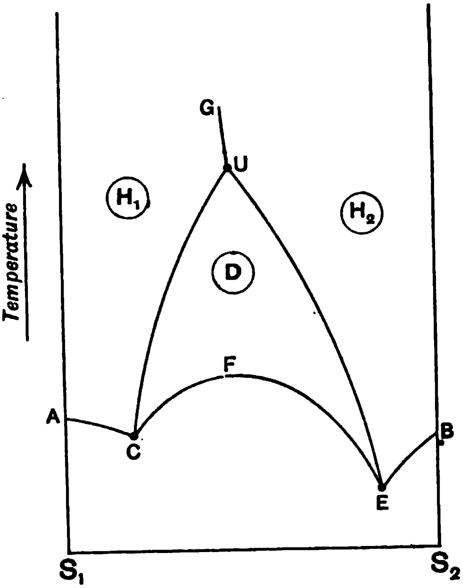
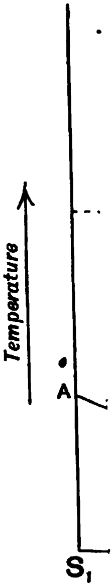


FIG 179.



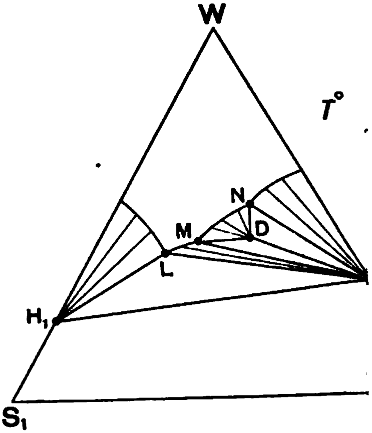


FIG. 182.

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in this case, the decomposition of the double salt hydrate into the two simple salt hydrates is accompanied by the liberation of a certain amount of water, the system formed by the two simple hydrates in equilibrium with solutions will be stable at comparatively higher temperatures, and that formed by the double salt hydrate in equilibrium with solutions will be stable at comparatively lower temperatures. A particular example of this case will occur when the double salt hydrate breaks down, not into two simple hydrates, but into the two anhydrous salts S_1 and S_2.

The polytherm in the system W–S_1–S_2 is represented in Figs. 178, 180, and 183, again as a projection of the space figure upon the base of the prism. We will first consider Fig. 178. Since, at low temperatures, the two hydrates H_1 and H_2 cannot both exist in equilibrium

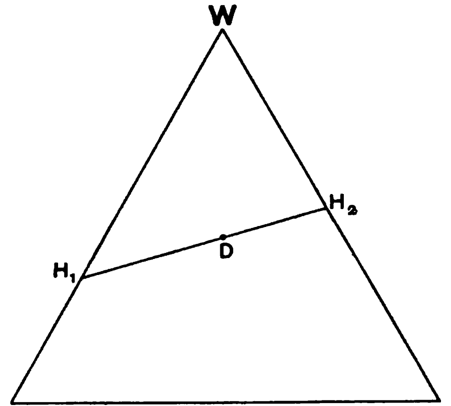


FIG. 175.

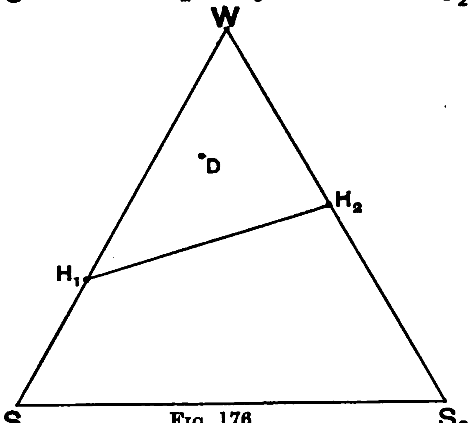


FIG. 176.

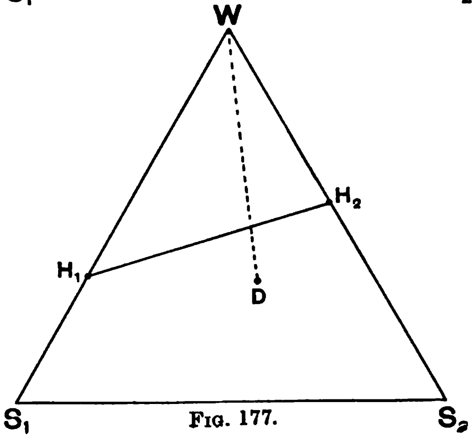


FIG. 177.

with saturated solutions, the two saturation curves *AC* and *BE*, of Ice + H_1 and of Ice + H_2 respectively, are separated by a third saturation curve *CE*—that of Ice + *D*. The two points *C* and *E* represent eutectic solutions in equilibrium with Ice + H_1 + *D* and Ice + H_2 + *D* respectively, for it is clear from the positions of these points that the phase equilibria existing at the corresponding temperatures are:

$$\text{Ice} + H_1 + D \rightleftarrows \text{Solution } C.$$
$$\text{Ice} + H_2 + D \rightleftarrows \text{Solution } E.$$

The saturation curve *CE*, of Ice + *D*, attains a temperature maximum at the point *F* where it intersects the straight line *WD*. This point represents a binary eutectic solution in equilibrium with Ice + *D* in the system *W–D*. This system is not actually a binary system since the line *WD* intersects, not only the saturation surfaces of ice and of *D*, but also that of H_2. It can, however, be considered as a binary system within a certain temperature range, namely, below the temperatures corresponding with the point *V*; in particular, the solution *D*, the composition of which can be expressed in positive terms of *W* and *D*, is in equilibrium with Ice + *D*, and it is, therefore, correctly described as a binary eutectic solution.

From each of the ternary eutectic points *C* and *E* three saturation curves diverge in the direction of rising temperature. The curve *CU* is the saturation curve of H_1 + *D*, *EU* that of H_2 + *D*, and they intersect in the point *U*, which represents the invariant solution in equilibrium with the three solid phases $H_1 + H_2 + D$. From this point, a third saturation curve *UG*, that of $H_1 + H_2$, diverges, and at higher temperatures the saturation curves and surfaces of the anhydrous salts S_1 and S_2 must appear. Fig. 178 shows only a part of the polytherm, namely the part WH_1H_2; the dehydration of the simple salt hydrates may occur in any of the ways which we have described in the previous paragraph, and we are concerned here only with the invariant equilibrium existing at the point *U*. The solution *U* is in equilibrium with the three solid phases H_1, H_2, *D* and it is incongruently saturated since the point *U* does not lie within the triangle H_1H_2D. Since, however, the point *D* lies within the triangle UH_1H_2, the composition of the double salt can be expressed in positive

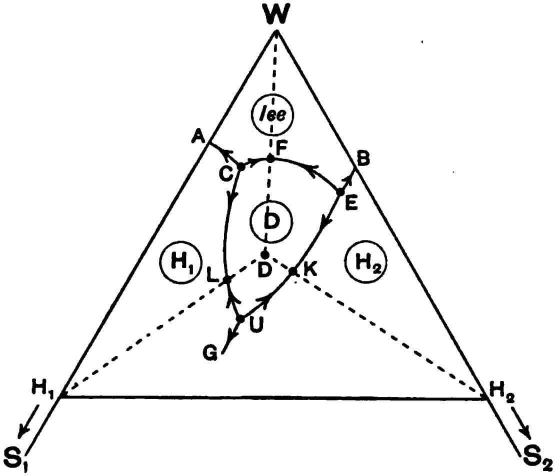
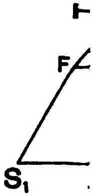


Fig. 183.



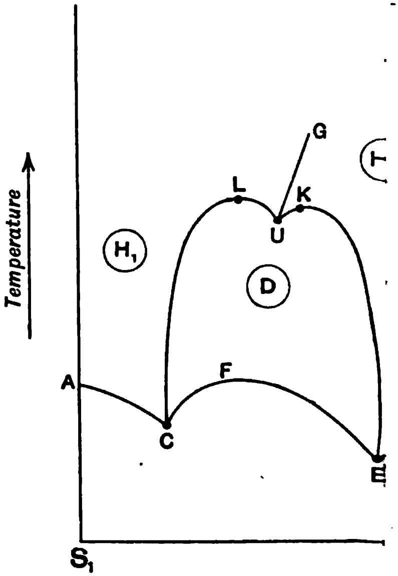


Fig. 184.

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terms of the two simple hydrates and the solution U; the equilibria existing at, and in the neighbourhood of, the invariant temperature are

$$D \rightleftarrows H_1 + H_2 + \text{Solution } U$$

$D + H_1 +$ Solution	
$D + H_2 +$ Solution	$H_1 + H_2 +$ Solution
$D + H_1 + H_2$	

Two saturation curves, those of $D + H_1$, and $D + H_2$, diverge from the point U in the direction of falling temperature, the third, that of $H_1 + H_2$, in the direction of rising temperature.

All these relations are correctly represented by the directions of the arrow-heads in Fig. 178, and by Jänecke's method in Fig. 179. This is the simplest case. The Jänecke polytherm is identical in type with that which represents a system in which an anhydrous double salt occurs (*cf.* Fig. 45); the isothermal types are correspondingly simple.

We will next suppose that the solution U is still incongruently saturated, but that the point which represents it is situated, with respect to the points H_1, H_2, D, as shown in Fig. 180. The point D does not, as in the previous case, lie within the triangle UH_1H_2, but the line UH_2 intersects the line DH_1. The equilibria existing at, and in the neighbourhood of, the invariant temperature are now:

$$D + H_1 \rightleftarrows H_2 + \text{Solution } U.$$

$D + H_1 +$ Solution	$H_1 + H_2 +$ Solution
$D + H_1 + H_2$	$D + H_2 +$ Solution

Only one saturation curve, that of $D + H_1$, diverges from the point U in the direction of falling temperature; the two others, those of $H_1 + H_2$ and $D + H_2$, do so in the direction of rising temperature. These relationships are correctly represented by the arrow-heads in Fig. 180, and by Jänecke's method in Fig. 181. The saturation curve UE, of $D + H_2$, diverges from both invariant points U and E in the direction of rising temperature, and it must, therefore, pass through a temperature maximum between the two; the point K represents this maximum, and in Fig. 180 it is given by the intersection of the saturation curve UE, of $H_2 + D$, with the straight line H_2D produced. It represents, in other words, a solution which is in equilibrium with both solid H_2 and solid

D, and the composition of which can be expressed in terms of H_2 and D alone; it is a true binary invariant point. Since, however, the point K does not lie between the points H_2 and D, the composition of the solution K cannot be expressed in positive terms of H_2 and D. The point K is not a binary eutectic point, but a binary transition point, and the phase reactions in equilibrium at the transition temperature are

$$D \rightleftarrows H_2 + \text{Solution } K.$$

An isotherm which is derived from the polythermal type of Figs. 180 and 181 is shown in Fig. 182. The constant temperature line T, in the Jänecke polytherm (Fig. 181), can be seen to cut the following saturation surfaces in order: those of H_1, H_2, D, H_2, and the isotherm shows the corresponding saturation curves in the same order. The saturation curve of H_2 is interrupted by that of D, and there are two isothermal invariant points M and N both representing solutions saturated at this temperature with $H_2 + D$. The isothermal saturation curve MN, of the hydrated double salt, is bounded at *each* end by that of H_2, whilst in the more usual case it is bounded (like the saturation curve of the anhydrous double salt) at one end by the saturation curve of one simple salt or simple salt hydrate, and at the other end by that of the second simple salt or hydrate.

Finally, we must consider the case in which the solution U is congruently saturated with the three solid phases H_1, H_2, and D. The point U then lies within the triangle H_1H_2D, as in Fig. 183, and the equilibria existing at, and in the neighbourhood of, the invariant temperature are

$$H_1 + H_2 + D \rightleftarrows \text{Solution } U$$

$$H_1 + H_2 + D \left| \begin{array}{l} H_2 + D + \text{Solution} \\ H_1 + D + \text{Solution} \\ H_1 + H_2 + \text{Solution.} \end{array} \right.$$

The point U is, in this case, a ternary eutectic point, and the three saturation curves of $H_2 + D$, $H_1 + D$ and $H_1 + H_2$, which diverge from it, all do so in the direction of rising temperature. The three invariant points C, E and U of Fig. 183, are now all eutectic points, and the arrow heads on the saturation curves in the neighbourhood of any one invariant point, are all directed away from that point. It is clear that both the saturation curves UC and UE, of H_1+D and H_2+D must now pass through temperature maxima at the points L and K, in which they intersect the straight lines H_1D and H_2D respectively. The Jänecke polytherm for this case is given in Fig. 184. A number of new isothermal types can be deduced from this polytherm, but we shall not discuss them in detail. The point D, which represents the hydrated double salt in Fig. 183, lies on the saturation surface of that salt. This means that a solution of the same composition as the hydrated double salt can exist in equilibrium with the solid double salt, or, in other words, that the latter has a stable melting point. If we imagine the space figure of which Fig. 183 is a projection (the temperature being measured vertically upwards, parallel to the edges of a triangular prism), we shall see that the saturation surface CEU, of the double salt, must attain a maximum within the prism, at the melting point of this salt; for the highest temperature at which solid double salt can exist in equilibrium with a liquid is the melting point of the pure salt, and the addition of another component must lower the temperature at which this equilibrium is possible. Since, then, this surface attains a maximum within the prism, an isothermal section of the space figure at a temperature slightly below the melting point of the hydrated double salt must intersect the surface in a closed curve which does not cut any face of the prism. The isothermal saturation curve of the hydrated double salt first appears, therefore, at the melting point of this salt, and it is represented in an isotherm slightly below this temperature, by a closed curve surrounding the point D. As the temperature falls, the saturation surface of the double salt in the polytherm will naturally intersect other surfaces, and the isothermal saturation curve will then cease to be a closed curve.

§ 90. We have seen in Chapter II. that the ternary isothermal saturation curve of a component (*e.g.*, that of ice) appears and disappears in the vertex which represents that component, at the melting temperature of the pure component. At a temperature slightly below the melting point, where the saturation curve as yet intersects no other curves, it is bounded by two sides of the triangle as, for example, is the curve AB of Fig 185. The corresponding conjugation lines include an angle of 60°. In the same way, we have seen (§ 88) that, if a binary compound such as a simple salt hydrate has a stable melting point, the isothermal saturation curve of that binary compound appears and disappears at the melting temperature, in the point which represents the compound. At a temperature slightly below the melting point, where the saturation curve as yet intersects no other curves, it is bounded by one side of the triangle as is, for example, the curve *CEF* of Fig. 185. The corresponding conjugation lines include an angle of 180°.

The isothermal saturation curve of a ternary compound, such as hydrated double salt, likewise appears and disappears at the melting point of that compound, when this point has a stable existence. At a temperature slightly below the melting point the isothermal saturation curve of the ternary compound is a closed curve which does not intersect any side of the triangle, and which completely surrounds the point representing the compound; such a curve is, for example, the curve *GKL* of Fig. 185, and the corresponding conjugation lines include an angle of 360°.

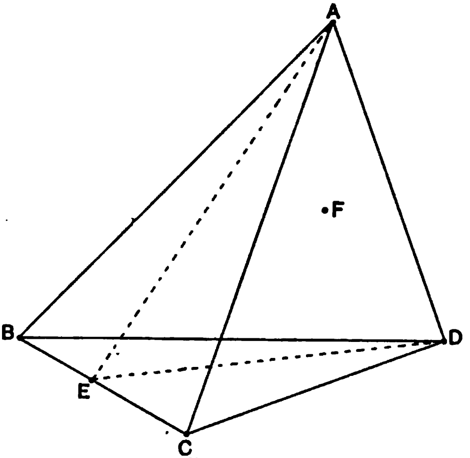


FIG. 186.

§ 91. The graphical deductions which deal with mixtures of two and of three phases can easily be extended to the case of quaternary mixtures. The four points *A*, *B*, *C*, *D* of Fig. 186 are supposed to be situated in space, and to represent the compositions of four phases, by reference to any three axes in space. We shall prove that a phase or complex which can be formed by mixing these four in any proportion, and the composition of which can, therefore, be expressed in positive terms of the four, is represented by a point within the tetrahedron *ABCD*. It follows from the deductions of the previous paragraphs that the point *E*, on the line *BC*, represents a mixture in the positive proportion CE/EB, of the two phases B and C. Points in the triangle ADE represent, therefore, all mixtures of the phases A, D, B, and C which contain the two latter in the fixed proportion represented by the point E. If the point E traverses the line BC, starting from B and ending at C, the proportion CE/EB will pass successively through all positive values, from $+\infty$ to 0, and the triangle ADE will generate the space included by the tetrahedron $ABCD$; all mixtures of the four phases A, B, C, and D, in any positive proportion, are represented, therefore, by points within the tetrahedron $ABCD$.

We shall now show that any point in space represents a phase or complex the composition of which can be expressed in terms of the four phases A, B, C, and D, but that those points which lie outside the tetrahedron $ABCD$ represent phases the compositions of which can be expressed in terms of A, B, C, and D only by the use of negative concentration values. Here, as with incongruent ternary phases, we must distinguish more than one case. The point G of Fig. 187, since it lies outside the tetrahedron $ABCD$, represents a phase or complex the composition of which cannot be expressed in positive terms of the four phases A, B, C, and D. When, however, the points G and B, G and C, G and D are joined by straight lines, it is found that the point A lies within the tetrahedron $GBCD$, and the composition of the phase A can, therefore, be expressed in positive terms of the four phases

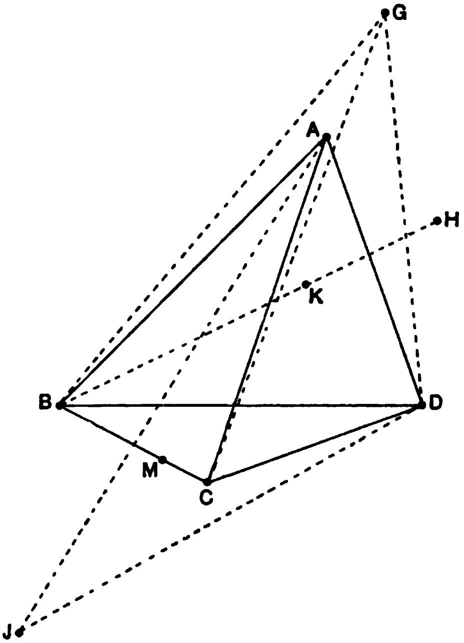


FIG. 187.

G, B, C, and D. We can represent this relation by the equation:

$$A = pG + qB + rC + sD,$$

where p, q, r, and s are positive numbers depending upon the position of the point A in the tetrahedron $GBCD$.

It follows that:

$$pG = A - qB - rC - sD,$$

and we see that the composition of the phase G can only be expressed in terms of the phases A, B, C, and D by assigning negative values to the concentrations of the *three* phases B, C, and D.

The point H (Fig. 187) also lies outside the tetrahedron $ABCD$, and also represents a phase which is incongruent with respect to the four phases A, B, C, and D. Further, it is impossible to construct a tetrahedron which shall contain the fifth point, by joining any four of the five points A, B, C, D, H. The incongruence of the phase H is of a different kind from that of the phase G. The straight line BH intersects the face ACD of the tetrahedron $ABCD$, and the point of intersection K represents a phase or complex the composition of which can be expressed in two ways. Since the point K lies on the straight line BH, the composition of the phase K can be expressed in positive terms of the two phases B and H:

$$K = pB + qH,$$

where p and q are positive numbers dependent upon the position of the point K on the line BH. Since this point also lies in the triangle ACD, it represents a phase the composition of which can be expressed in positive terms of the three phases A, C, and D:

$$K = rA + sC + tD,$$

where r, s, and t are positive numbers dependent upon the position of the point K in the triangle ACD.

These two expressions for the composition of the phase K must be identical, and we obtain the following expression which relates the compositions of the five phases A, B, C, D, and H:

$$pB + qH = rA + sC + tD$$

or

$$qH = rA + sC + tD - pB.$$

We see that the composition of the phase H can be expressed in terms of the phases A, B, C, and D by assigning a negative value to the concentration of *one* phase, that of the phase B.

There is a third case, which is exemplified by the point J of Fig. 187; both the lines JA and JD are supposed to lie wholly outside the tetrahedron $ABCD$, and they do not, therefore, intersect any tetrahedral face. In this case, the plane triangle JAD intersects the side BC of the tetrahedron, and the point of intersection M represents a phase or complex the composition of which can be expressed in two ways; since the point M lies on the straight line BC, we can write:

$$M = pB + qC,$$

and since it also lies in the triangle JAD,

$$M = rJ + sA + tD.$$

We have, therefore, the following expression, which relates the compositions of the five phases A, B, C, D, and J

$$pB + qC = rJ + sA + tD$$

or

$$rJ = pB + qC - sA - tD$$

The point J represents, then, a phase or complex the composition of which can be expressed in terms of the four phases A, B, C, and D by assigning a negative value to the concentrations of *two* of them, namely A and D.

It is clear that, if the points A, B, C, and D represent the compositions of four solid phases, and the points F of Fig. 186, G, H, and J of Fig. 187, the compositions of liquid phases in invariant equilibrium with these, the phase reactions which occur, in each of the four cases, when heat is added to, or removed from, the invariant system, are

$$A + B + C + D \rightleftarrows \text{Solution } F$$
$$A \rightleftarrows B + C + D + \text{Solution } G$$
$$A + C + D \rightleftarrows B + \text{Solution H}$$

and

$$B + C \rightleftarrows A + D + \text{Solution } J, \text{ respectively.}$$

The point F will be a quaternary eutectic point; the points G, H, and J, which represent incongruently saturated invariant solutions, will be quaternary transition points.

§ 92. As an example of the graphical methods described in the previous paragraph, we will first consider the relations existing at the quaternary isothermal invariant point. For this purpose, we will refer to Fig. 116 of Chapter III. This figure represents an isotherm in the quaternary system formed by water and the reciprocal salt pairs $(\overset{+}{A}, \overset{+}{C})$–$(\overset{-}{B}, \overset{-}{D})$, and it may be considered as the projection of a space figure referred to a pyramid W,AD,AB,BC,CD, the vertex W of which represents pure water and lies above the plane of the paper (the pyramid of Fig. 110). The point p represents an isothermal invariant solution which is in equilibrium with the three solid salts AB, AD, and CD, and this solution is congruently saturated if its composition can be expressed in positive terms of water and these three salts (we have described an *isothermal* invariant solution as being congruently saturated when it is congruent with respect to *water and* the solid phases with which it is in equilibrium (§ 86)). Since the point p of Fig. 116 lies within the triangle AB, AD, CD, it is clear that the point of which p is the projection must lie within the tetrahedron W, AB, AD, CD in the space figure of which Fig. 116 is the projection. The solution p is, therefore, congruently saturated, and we can write :

$$\text{Solution } p = mAB + nAD + sCD + tW.$$

This expression is merely a mathematical relation between the compositions of the five phases p, AB, AD, CD, W. It acquires a physical significance if we suppose water to be removed from the invariant system, for in this case a phase reaction must occur which maintains the constant composition of the solution, and this reaction is

$$\text{Solution } p \longrightarrow AB + AD + CD + W \text{ (removed)}.$$

If the removal of water is continued, the reaction will proceed until the liquid phase has disappeared, and there will remain only the completely solid system : $AB + AD + CD$. The point p is, therefore, a drying-up point.

The point q represents the isothermal invariant solution which is in equilibrium with the three salts AB, BC, and CD, but since it lies outside the triangle AB, BC, CD, the solution q is incongruently saturated. It is clear that, in the space figure of which Fig. 116 is a projection, the point which corresponds to q must be so situated with respect to the tetrahedron W, AB, BC, CD that the straight line q,BC intersects the face W,AB,CD. The relation between the compositions of the five phases q, AB, BC, CD, W is, therefore, of the form (§ 91).

$$\text{Solution } q + mBC = nAB + sCD + tW,$$

and if water is removed from the invariant system, the composition of the liquid phase can only be maintained constant by the following phase reaction:

$$\text{Solution } q + BC \rightarrow AB + CD + W \text{ (removed).}$$

We see that when water is evaporated from the isothermal invariant system Solution $q + BC + AB + CD$, the two salts AB and CD are alone deposited from the solution, whilst the third salt BC is dissolved by it. In the presence of sufficient of the liquid phase, this reaction will ultimately lead to the complete disappearance of the solid phase BC, and the formation of the isothermal monovariant system: Solution + $AB + CD$. The continued removal of water will therefore cause the point which represents the composition of the solution to move from q, along the saturation curve qp, of $AB + CD$; the point q is, in other words, not a drying-up point. We have already deduced this behaviour in § 74.

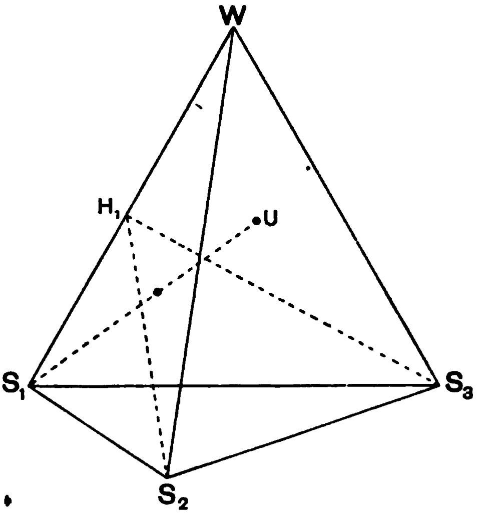


FIG. 188.

The various quaternary polythermal types which may arise, when a binary or ternary compound occurs as a solid phase in the system, can be studied, and the possible quaternary isothermal types can be deduced, by means of these graphical methods.

We have seen that, when a simple salt hydrate occurs as a solid phase, the possible isothermal types in the ternary system are very numerous, and they are greatly increased in the quaternary system. We can do no more than indicate the way in which these types can be deduced. The isotherm in the quaternary system W–S_1–S_2–S_3 can be represented within the tetrahedron $WS_1S_2S_3$ of Fig. 188. A hydrate H_1 occurs in the binary system W–S_1, and its composition is represented by the point H_1 on the side WS_1 of the tetrahedron. At a temperature sufficiently low, the anhydrous salt S_1 will be incapable of existing as a solid phase in the system, and the only solid phases which can occur (excluding ice) are the two anhydrous salts S_2 and S_3, and the hydrate H_1. If the temperature is gradually raised, a point will be reached at which dehydration of the hydrate begins, and this point will be the quaternary system invariant point at which the four phases $S_2 + S_3 + H_1 + S_1$ are all in equilibrium with a quaternary invariant solution. We will suppose that the point U of Fig. 188 represents the composition of the invariant solution which is in equilibrium with the four solid phases represented by the points S_2, S_3, H_1, and S_1. The straight line US_1 intersects the face $H_1S_2S_3$ of the tetrahedron $H_1S_1S_2S_3$, and the equilibria existing at, and in the neighbourhood of, the invariant temperature are (§ 91).

$$H_1 + S_2 + S_3 \rightleftharpoons S_1 + \text{Solution } U$$

$$\begin{array}{l|l}
H_1 + S_2 + S_3 + \text{Solution} & H_1 + S_2 + S_1 + \text{Solution} \\
 & H_1 + S_3 + S_1 + \text{Solution} \\
H_1 + S_2 + S_3 + S_1 & S_2 + S_3 + S_1 + \text{Solution}
\end{array}$$

The point U is a quaternary transition point—the transition point of the hydrate in the quaternary system. We have already discussed this case, and the corresponding isothermal types, in § 58. One polythermal saturation curve—that of $H_1 + S_2 + S_3$—diverges from the transition point in the direction of falling temperature, and isotherms at temperatures immediately below that of the transition point will show, therefore, one isothermal invariant point, namely, a point which represents a solution saturated with the three solids $H_1 + S_2 + S_3$; this isothermal type was illustrated in Fig. 86 of § 58. Three polythermal saturation curves diverge from the transition point in the direction of rising temperature, namely, those of $H_1 + S_2 + S_1$, $H_1 + S_3 + S_1$ and $S_2 + S_3 + S_1$.

The isotherm at temperatures immediately above the transition point will contain, therefore, the three corresponding isothermal invariant points, and these are shown by Fig. 88 of § 58; the saturation surface of the anhydrous salt S_1, when it first appears, cuts the three remaining saturation surfaces around their common point of intersection.

We will next suppose that the point U, which represents the quaternary invariant solution in equilibrium with the four solid phases H_1, S_1, S_2, S_3, lies within the tetrahedron $H_1S_1S_2S_3$, as shown in Fig. 189. The equilibria existing at, and in the neighbourhood of, the invariant temperature are, in this case

$$H_1 + S_1 + S_2 + S_3 \rightleftarrows \text{Solution } U$$

$$H_1 + S_1 + S_2 + S_3 \left| \begin{array}{ll} H_1 + S_1 + S_2 + \text{Solution} \quad . & (1). \\ H_1 + S_1 + S_3 + \text{Solution} \quad . & (2). \\ H_1 + S_2 + S_3 + \text{Solution} \quad . & (3). \\ S_1 + S_2 + S_3 + \text{Solution} \quad . & (4). \end{array} \right.$$

The point U is a quaternary eutectic point, and we shall find that the relations which exist in this case are strictly analogous to those which exist in the ternary system discussed in § 88, in which the invariant system $H_1 + S_1 + S_2 +$ Solution characterised a ternary eutectic point. Four polythermal saturation curves diverge from the point U, all in the direction of rising temperature, and at a temperature immediately above this eutectic point, an isotherm must contain the four isothermal invariant points which correspond with the monovariant systems 1, 2, 3, and 4.

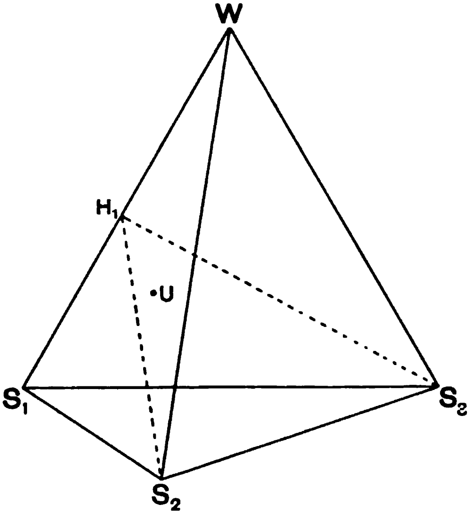


FIG. 189.

Since ice can also appear as a solid phase, the quaternary system must possess a second eutectic point at some lower temperature. The anhydrous salt S_1 will be incapable of existing at this low temperature, and the four solid phases in equilibrium with the invariant liquid (which we will call Solution X) at this second eutectic point will therefore be ice, H_1, S_2, S_3; the equilibria existing at, and in the neighbourhood of, the eutectic temperature will be

$$\text{Ice} + H_1 + S_2 + S_3 \rightleftarrows \text{Solution } X$$

$$\text{Ice} + H_1 + S_2 + S_3 \left|\begin{array}{lr} \text{Ice} + H_1 + S_2 + \text{Solution} \quad . & (5). \\ \text{Ice} + H_1 + S_3 + \text{Solution} \quad . & (6). \\ \text{Ice} + S_2 + S_3 + \text{Solution} \quad . & (7). \\ H_1 + S_2 + S_3 + \text{Solution} \quad . & (8). \end{array}\right.$$

It can be seen that the monovariant system

$$H_1 + S_2 + S_3 + \text{Solution}$$

(3 and 8) exists at temperatures immediately above both eutectic points X and U. The polythermal saturation curve of $H_1 + S_2 + S_3$ must diverge, therefore, both from the invariant point X and the invariant point U in the direction of rising temperature, and between the two it must pass through a temperature maximum. A plane of constant temperature in a polytherm represented, for example, by the method described in § 57 must cut the saturation curve of $H_1 + S_2 + S_3$, at a temperature immediately above that of the higher eutectic point U, in two points—one on each side of the maximum. The isotherm will then contain in addition to the isothermal invariant points which correspond to the monovariant systems 1, 2, and 4, *two* invariant points which represent solutions in equilibrium with $H_1 + S_2 + S_3$, and which correspond to the monovariant systems 3 and 8.

The maximum in the polythermal saturation curve of $H_1 + S_2 + S_3$ must be given by a point which represents a solution the composition of which can be expressed in terms of H_1, S_2, S_3 alone, *i.e.*, by an invariant point in the ternary system H_1–S_2–S_3. The isotherm in this ternary system would be represented, not in any of the faces of the tetrahedron in Fig. 189, but in the plane triangular section $H_1S_2S_3$ of this figure, and we can consider the quaternary system W–S_1–S_2–S_3, in the case we are considering, as built up of the two independent and simpler systems W–H_1–S_2–S_3 and S_1–H_1–S_2–S_3; each of these

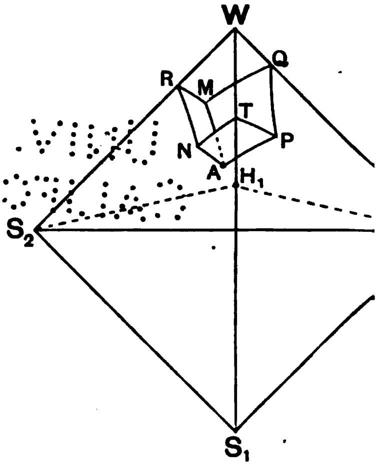


Fig. 190.

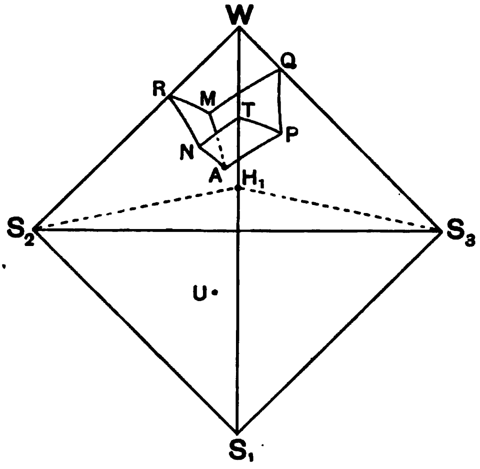
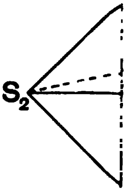


Fig. 191.



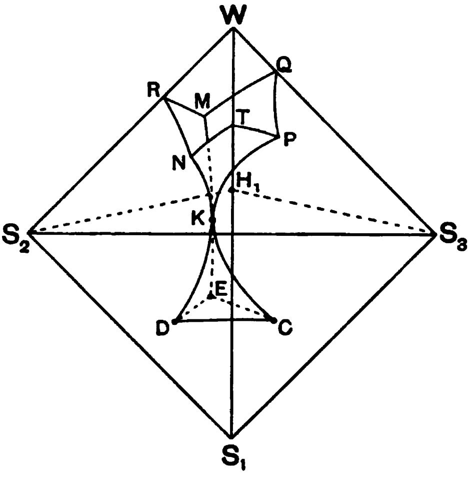
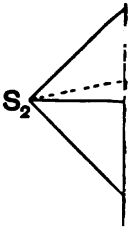


Fig 193.



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systems possesses one eutectic point only—the points X and U respectively—which represent solutions in equilibrium with the four solid components Ice $+H_1+S_2+S_3$ and $S_1+H_1+S_2+S_3$. The isotherms in the two simpler systems will be represented within the tetrahedra $WH_1S_2S_3$ and $H_1S_1S_2S_3$, which together form the tetrahedron $WS_1S_2S_3$ of Fig. 189.

For the discussion of the isothermal types, we shall here use a projection of the space isotherm upon a plane parallel to the pair of opposite tetrahedral edges WS_1 and S_2S_3, as shown in Fig. 190 (*cf.* § 54). This figure represents the isotherm at a temperature above the melting point of ice, and below the temperature of the eutectic point U in the system H_1–S_1–S_2–S_3. All mixtures in this system must therefore be completely solid, and no saturation surface can extend into the tetrahedron $S_1H_1S_2S_3$ of Fig. 190. The system W–H_1–S_2–S_3 is of simple type, and shows only the saturation surfaces of H_1, S_2, and S_3 (since the temperature is above the melting point of ice, this solid phase cannot appear). The three saturation surfaces intersect in the isothermal invariant point A, which represents a solution saturated with all three solid phases $H_1+S_2+S_3$.

When the temperature is raised, the isothermal type will remain unaltered until the temperature of the eutectic point U is reached. At this temperature, one solution can exist in the system S_1–H_1–S_2–S_3, namely, the invariant solution in equilibrium with the four solid components $S_1+H_1+S_2+S_3$. At a slightly higher temperature, this system invariant point will be replaced by four isothermal saturation surfaces, the saturation surfaces of the separate components S_1, H_1, S_2, S_3; in the same way, for example, the ternary eutectic point M of Fig. 168 was replaced in Fig. 169 by the three isothermal saturation curves of the separate components.

The quaternary isotherm at the temperature of the eutectic point U is represented in Fig. 191, and at a slightly higher temperature in Fig. 192. The system invariant point U of Fig. 190 has expanded in Fig. 192, into a tetrahedron $BCDE$, the faces of which are the saturation surfaces of the separate components S_1, H_1, S_2, and S_3. We can compare these figures with the corresponding ternary isotherms (Figs. 168 and 169), in which the system invariant point M expands into the triangle *LJB*, whose sides are the saturation curves of the separate components.

The isothermal type of Fig. 192 contains the five isothermal invariant points the existence of which, at a temperature slightly above that of the eutectic point *U*, has been already deduced. Both the isothermal invariant points *A* and *B* of this figure represent solutions in equilibrium with the three solids $H_1+S_2+S_3$, and we have seen that their presence is due to the existence of a temperature maximum in the polythermal saturation curve of $H_1+S_2+S_3$. As the temperature is still further raised, the two points *A* and *B* must approach one another and eventually coincide at the temperature of this maximum point. The latter represents, as we have seen, a ternary invariant point in the system H_1–S_2–S_3, and the points *A* and *B* of Fig. 192 must, therefore, reach coincidence at a point in the plane triangle $H_1S_2S_3$; the corresponding isothermal transition form may be represented by Fig. 193. The point *K* lies in the plane of the triangle $H_1S_2S_3$, and represents the eutectic point in the ternary system H_1–S_2–S_3. The surfaces *TNAP* and *BDC* in Fig. 192, are the quaternary saturation surfaces of the hydrate in the systems W–H_1–S_2–S_3 and S_1–H_1–S_2–S_3 respectively; in the transition form (Fig. 193), these two surfaces have met, and they now form one continuous saturation surface *TNKDCKP*. Similarly, the saturation surfaces *RNAM* and *BDE*, of S_2 in Fig. 192, are replaced by the continuous surface *RNKDEKM* in Fig. 193, the saturation surfaces *QPAM* and *BCE*, of S_3, are replaced by the continuous surface *QPKCEKM*.

The temperature of the eutectic point in the ternary system H_1–S_2–S_3 is the highest temperature at which the three solids H_1, S_2, and S_3 can exist in equilibrium with a solution. At temperatures above that which corresponds to Fig. 193, the saturation surfaces of H_1, S_2, and S_3 can have, therefore, no common point of intersection. The isothermal type is then given by Fig. 194, and the intersection *XYZ*, of the quaternary saturation surfaces with the plane $H_1S_2S_3$, gives the isotherm in the ternary system H_1–S_2–S_3 at this temperature.

As the temperature is further raised, the isothermal invariant points *D* and *C* will approach the faces WS_1S_2 and WS_1S_3, of the tetrahedron. They will reach these faces at the corres-

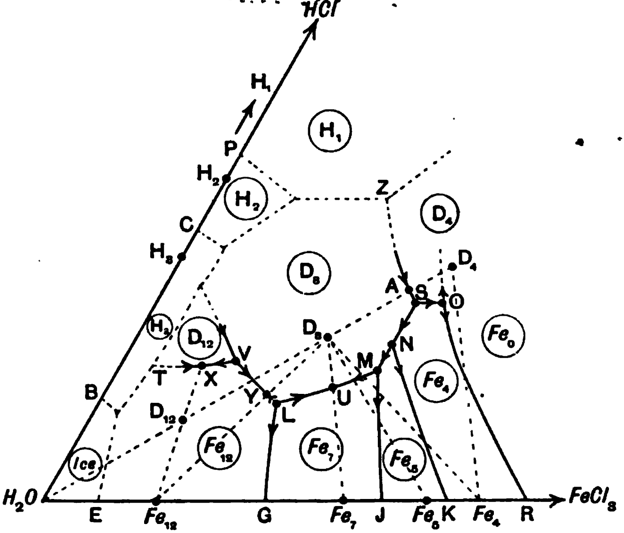

Fig. 195.

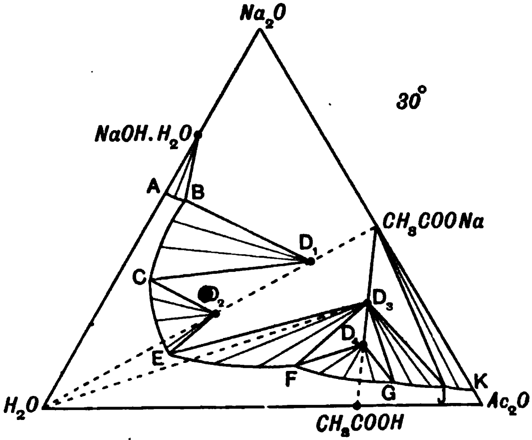

Fig. 197.

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ponding invariant temperatures in the ternary systems W–S_1–S_2 and W–S_1–S_3 (the temperatures at which $H_1+S_1+S_2$ and $H_1+S_1+S_3$ can exist in equilibrium with ternary invariant solutions). We have assumed that the eutectic temperature in the ternary system H_1–S_2–S_3 is lower than either of these, for it is only in this case that the point B of Fig. 192 will reach the triangle $H_1S_2S_3$ before either of the points D or C reach the faces of the tetrahedron. Other isothermal types will occur at temperatures above those of the ternary invariant equilibria

$$H_1+S_1+S_2+\text{Ternary Solution}$$

and

$$H_1+S_1+S_3+\text{Ternary Solution.}$$

We leave these to be deduced by the reader.

§ 93. The ternary system H_2O–HCl–$FeCl_3$[1] offers examples of some of the polythermal and isothermal types which we discussed in §§ 87 and 88. The polytherm in this system is represented diagrammatically, in Fig. 195, as a projection of the space figure upon the triangular base of the prism. A part only of the triangle H_2O, HCl, $FeCl_3$ is shown in this figure, and those polythermal saturation curves which have been experimentally determined are drawn in full line, whilst the dotted saturation curves are hypothetical.

The binary system H_2O–HCl is represented on the side H_2O.HCl of the triangle, and the three hydrates $HCl.3H_2O$, $HCl.2H_2O$, and $HCl.H_2O$ occur as solid phases; they will be denoted by the symbols H_3, H_2, and H_1 respectively, and their compositions are given by the points H_3, H_2, H_1 on the side of the triangle in Fig. 195. The point B represents the binary eutectic solution which is in equilibrium with ice and the trihydrate H_3. The part BC, of the side of the triangle, represents the binary saturation curve of this hydrate, and the point H_3, since it lies on this curve, represents a liquid of the same composition as the trihydrate in equilibrium with the solid hydrate. The trihydrate possesses, in other words, a stable melting point represented by the point H_3; and the point C, which represents the binary invariant solution in equilibrium with both the trihydrate and the dihydrate, is, therefore, a eutectic point. The dihydrate also possesses a stable melting point, represented by the point H_2; and the point P, which

[1] Roozeboom and Schreinemakers, *Zeitsch. physikal. Chem.*, 1894, **15**, 588.

represents the invariant solution in equilibrium with both the dihydrate and the monohydrate H_1, forms a third binary eutectic point. These invariant equilibria and the corresponding invariant temperatures are given below:

At the stable melting point :

H_3	Solid $H_3 \rightleftarrows$ Liquid H_3	$-24 \cdot 9°$
H_2	Solid $H_2 \rightleftarrows$ Liquid H_2	$-17 \cdot 7°$

At the binary eutectic point :

B	Ice + $H_3 \rightleftarrows$ Solution B	$-86°$
C	$H_3 + H_2 \rightleftarrows$ Solution C	$-35°$
P	$H_2 + H_1 \rightleftarrows$ Solution P	$-20°$.

The binary system H_2O–$FeCl_3$ is represented on the side H_2O,$FeCl_3$ of the triangle, and several hydrates appear in this system. Besides ice, the following solid phases can occur :

$Fe_2Cl_6.12H_2O$ denoted by Fe_{12}
$Fe_2Cl_6.7H_2O$,, Fe_7
$Fe_2Cl_6.5H_2O$,, Fe_5
$Fe_2Cl_6.4H_2O$,, Fe_4
Fe_2Cl_6 ,, Fe_0.

It can be seen from the figure that each of these hydrates possesses a stable melting point, and every invariant point in this binary system is, therefore, a eutectic point. The phase equilibria existing at these invariant points, and the corresponding invariant temperatures, are the following :

At the stable melting point

Fe_{12}	Solid $Fe_{12} \rightleftarrows$ Liquid Fe_{12}	37°
Fe_7	Solid $Fe_7 \rightleftarrows$ Liquid Fe_7	32·5°
Fe_5	Solid $Fe_5 \rightleftarrows$ Liquid Fe_5	56°
Fe_4	Solid $Fe_4 \rightleftarrows$ Liquid Fe_4	73·5°

At the binary eutectic point

E	Ice + $Fe_{12} \rightleftarrows$ Solution E	$-55°$
G	$Fe_{12} + Fe_7 \rightleftarrows$ Solution G	27·4°
J	$Fe_7 + Fe_5 \rightleftarrows$ Solution J	30°
K	$Fe_5 + Fe_4 \rightleftarrows$ Solution K	55°
R	$Fe_4 + Fe_0 \rightleftarrows$ Solution R	66°

The ternary saturation surfaces of ice, the hydrates of hydrochloric acid, and the hydrates of ferric chloride are marked with the corresponding symbols in Fig. 195. Besides these, there are three ternary compounds which can occur as solid phases in the system; they are:

$Fe_2Cl_6.2HCl.12H_2O$ denoted by D_{12}
$Fe_2Cl_6.2HCl.8H_2O$,, D_8
$Fe_2Cl_6.2HCl.4H_2O$,, D_4,

and their compositions are given by the points D_{12}, D_8, and D_4 in the figure. The saturation surfaces of these compounds are restricted to the interior of the triangle, and they are also marked with the corresponding symbols.

It can be seen that the point D_8, which represents the solid compound $Fe_2Cl_6.2HCl.8H_2O$, lies on the saturation surface of the compound, and it therefore possesses a stable melting point, at which it is in equilibrium with a liquid phase of identical composition with it:

$$\text{Solid } D_8 \rightleftarrows \text{Liquid } D_8 \quad . \quad . \quad . \quad . \quad . \quad -3°.$$

The point D_{12} does not lie on the saturation surface of D_{12}, nor the point D_4 on the saturation surface of D_4, and these two ternary compounds do not, therefore, possess stable melting points.

The polythermal saturation surfaces are bounded by polythermal saturation curves, the significance of which can be read from the figure. The curve TV is the saturation curve of $Fe_{12} + D_{12}$, and, since it intersects the straight line Fe_{12}, D_{12} produced, it passes through a temperature maximum. The point of intersection X lies on this straight line, and represents, therefore, a solution the composition of which can be expressed in terms of Fe_{12} and D_{12} alone. It is clearly a binary invariant point, but since it does not lie between the points Fe_{12} and D_{12}, it is a transition point, and not a eutectic point; it is the point of maximum temperature on the curve TV. From the positions of the points Fe_{12}, D_{12}, and X, it follows that the phase reactions in equilibrium at this binary transition point are

$$D_{12} \rightleftarrows Fe_{12} + \text{Solution } X \quad . \quad . \quad . \quad . \quad -12{\cdot}5°$$

If the solid ternary compound $Fe_2Cl_6.2HCl.12H_2O$ is heated, it will, therefore, break down at a temperature of − 12·5°, into the binary compound $Fe_2Cl_6.12H_2O$ and a liquid phase of the composition represented by the point X. This behaviour is to be contrasted with that of the ternary compound D_8, which possesses a stable melting point; when the solid D_8 is heated it melts at a temperature of − 3°, to a liquid of identical composition with it.

It will be seen that the saturation curves VL, LM, and SZ, of $D_8 + Fe_{12}$, $D_8 + Fe_7$, and $D_8 + D_4$ respectively, all pass through temperature maxima, which represent, in these cases, binary eutectic points. It be will found from the figure that the phase equilibria existing at these invariant points are the following:

At the binary eutectic point:

Y $D_8 + Fe_{12} \rightleftarrows$ Solution Y
U $D_8 + Fe_7 \rightleftarrows$ Solution U . . . − 4·5°
A $D_8 + D_4 \rightleftarrows$ Solution A . . . − 26·5°

The system formed by the two compounds D_8 and Fe_7 behaves as a true binary system, for the straight line D_8Fe_7 intersects only the saturation surfaces of D_8 and Fe_7, and the saturation curve of $D_8 + Fe_7$. The melting point of the pure substance D_8 is − 3°, that of the pure substance Fe_7, 32·5°, whilst the temperature of the binary eutectic point U, *i.e.*, the common melting point of D_8 and Fe_7, is − 4·5°. The system $D_8 - Fe_{12}$ is, similarly, a true binary system, but the system $D_8 - D_4$ does not behave as a binary system through the whole temperature range, since a small part of the straight line D_8D_4 lies on the saturation surface of Fe_0.

It can be seen that the saturation curves MN, NS, and SO do not attain their temperature maxima in stable regions.

The polythermal saturation curves run together, in groups of three, in the ternary invariant points. The point L represents the ternary invariant solution in equilibrium with the three solid phases D_8, Fe_{12}, and Fe_7, and from its position within the triangle D_8, Fe_{12}, Fe_7, it follows that the phase reactions in equilibrium are:

$D_8 + Fe_{12} + Fe_7 \rightleftarrows$ Solution L . . . − 7·5°.

The point L is, therefore, a ternary eutectic point. The point S is a second ternary eutectic point, for the phase reactions in equilibrium are:

$D_4 + D_8 + Fe_4 \rightleftarrows$ Solution S . . . − 27·5°.

The remaining ternary invariant points which have been experimentally determined are all transition points, and the phase reactions which are in equilibrium at these points can be readily determined from the figure. They are given below, together with the corresponding transition temperatures :

At the ternary transition point

V	$D_8 + D_{12} \rightleftarrows \mathrm{Fe}_{12} +$ Solution *V* . .	$-13°$.
M	$D_8 + \mathrm{Fe}_5 \rightleftarrows \mathrm{Fe}_7 +$ Solution *M* . .	$-7{\cdot}3°$.
N	$D_8 + \mathrm{Fe}_4 \rightleftarrows \mathrm{Fe}_5 +$ Solution *N* . .	$-16°$.
O	$D_4 + \mathrm{Fe}_4 \rightleftarrows \mathrm{Fe}_0 +$ Solution *O* . .	29°.

We have seen that the simple salt hydrate

$$\mathrm{Fe_2Cl_6.12H_2O}\ (\mathrm{Fe}_{12})$$

which occurs as a solid phase in this system, possesses a stable melting point at 37°. Between this temperature and 27·4°, the ternary saturation curve of this hydrate, in the system $\mathrm{H_2O}$–HCl–$\mathrm{FeCl_3}$, possesses the form which we deduced in § 88 for the ternary saturation curve of a simple hydrate, at a temperature immediately below its melting point. It is given by the curve *ABCDEF* of Fig. 196, which surrounds the point Fe_{12}, and is bounded at each end, by the side $\mathrm{H_2O,FeCl_3}$ of the triangle. Every point on this saturation curve may be joined by a conjugation line to the point Fe_{12}, which gives the composition of the solid phase in equilibrium with saturated solutions represented by points on the curve. Every point in the area generated by the conjugation lines then represents a phase complex of the solid hydrate Fe_{12} with a saturated solution. The point *E* lies on this saturation curve, and represents, therefore, a solution just saturated with the hydrate F_{12}. If a small amount of water is added to this solution, the composition of the resulting mixture will be represented by a point such as *G*, which lies in the complex area $\mathrm{Fe}_{12}+$ Solution. The point *G* represents a phase complex of the solid hydrate Fe_{12} and the saturated solution *D*. If still more water is added, the composition of the mixture may be represented by the point *J*, and the mixture itself will then form a complex of the solid hydrate and the saturated solution *C*. When so much water has been added that the composition of the resulting mixture is given by the point *B*, there will again be formed a solution which is just saturated with the hydrate, and the further addition of water will yield unsaturated solutions represented by points on the line H_2O,*B*. We see that when water is added in increasing amounts to the saturated solution *E*, the solid hydrate $Fe_2Cl_6.12H_2O$ is first precipitated. The point representing the composition of the solution traverses the saturation curve from *E* to *B*, and a second solution is eventually obtained which is also just saturated with the hydrate.

The ternary compound $Fe_2Cl_6.2HCl.8H_2O$ (D_8) has a stable melting point at − 3°, and its saturation curve in the ternary system H_2O–HCl–$FeCl_3$, between − 3° and − 4·5°, has the form which we deduced in § 89 for the saturation curve of a ternary compound at a temperature immediately below its melting point. It is given by the closed curve *KMLN* of Fig. 196, which completely surrounds the point D_8. The straight lines H_2O,*K*, and H_2O,*L* are the tangents to this curve, from the point H_2O, and it is clear that if water is added to a solution represented by a point on the part *KML* of the saturation curve, an unsaturated solution will immediately result. If, on the other hand, water is added to a solution represented by a point on the part *KNL*, a phase complex of the solid compound with a saturated solution will first be be formed. As more water is added, the point representing the composition of the solution in this phase complex will traverse a part of the saturation curve, and a second solution just saturated with the compound will be obtained before the point enters the area of unsaturated solutions. The behaviour of the solution *N* is peculiar. On the addition of water to this solution, the solid compound D_8 will be precipitated, and the point representing the composition of the resulting complex will traverse the line ND_8. The actual composition of the solution will therefore remain unaltered at the value represented by the point *N*; the amount of the solid phase will increase at the expense of that of the liquid phase (the composition of which remains constant), until, when so much water has been added that the composition of the mixture is represented by the point D_8 itself, the liquid phase will have solidified completely to the dry compound D_8. The further addition of water will again result in the formation of phase complexes, represented now by points on the line D_3M; they consist of solid D_3 in equilibrium with the saturated solution M. The composition of the solution remains unaltered as water is added, but its amount increases at the expense of that of the solid phase, until the latter has disappeared entirely when the composition of the mixture is itself represented by the point M. The subsequent addition of water will result in the formation of unsaturated solutions.

An example of an isothermal type deduced in § 89 (Fig. 182), for the case in which a ternary compound occurs as a solid phase, is offered by the system H_2O–Na_2O–$(CH_3CO)_2O$ at 30°.[1] This isotherm is shown in Fig. 197. As solid phases, there occur a number of hydrated compounds of sodium oxide and acetic anhydride, namely two neutral sodium acetates and two acid sodium acetates. The compositions of these compounds are given below, and they are represented in Fig. 196, by the points D_1, D_2, D_3, and D_4; the abbreviated symbol Ac_2O is used for acetic anhydride.

$Na_2O.Ac_2O.H_2O$ (or $CH_3COONa.\frac{1}{2}H_2O$) is denoted by D_1,
$Na_2O.Ac_2O.6H_2O$ (or $CH_3COONa.3H_2O$) is denoted by D_2,
$Na_2O.2Ac_2O.H_2O$ (or $CH_3COONa.CH_3COOH$) is denoted by D_3,
$Na_2O.3Ac_2O.2H_2O$ (or $CH_3COONa.2CH_3COOH$) is denoted by D_4.

It can be seen that the saturation curve of the acid acetate D_3 is interrupted by that of D_4. The two branches EF and GJ both represent a series of solutions saturated with D_3, and they are completely separated by the curve FG, the points of which represent solutions saturated with D_4. The two isothermal invariant points F and G both represent solutions saturated at 30°, with the two acid salts D_3 and D_4.

A somewhat similar behaviour is found in the system H_2O–Li_2SO_4–$LiNO_3$ at 35°,[2] and the isotherm in this system is shown in Fig. 198. The stable solid phase in the binary system H_2O–Li_2SO_4 at this temperature is the monohydrate $Li_2SO_4.H_2O$. The ternary saturation curve of this hydrate is represented, however, by two branches *AB* and *DE*, which are completely separated by the saturation curves of *two* hydrated double salts :

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[1] Dukelski, *Zeitsch. physikal. Chem.*, 1909, **62**, 114.

[2] Massink, *Zeitsch. physikal. Chem.*, 1917, **92**, 357.

$9Li_2SO_4.LiNO_3.27H_2O$ denoted by D_1,
and $11Li_2SO_4.LiNO_3.17H_2O$,, D_2.

The simple hydrate $Li_2SO_4.H_2O$ can exist, therefore, at the same temperature, in equilibrium with the ternary compound D_1 and a saturated solution (*B*), and with the ternary compound D_2, and a saturated solution (*D*).

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